Tomography-based characterization of porous media applied to snow, bone scaffolds and reticulated ceramics

Author(s):
Zermatten, Emilie

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TOMOGRAPHY-BASED CHARACTERIZATION OF POROUS MEDIA APPLIED TO SNOW, BONE SCAFFOLDS AND RETICULATED CERAMICS

A thesis submitted to attain the degree of DOCTOR OF SCIENCES of ETH ZURICH (Dr. sc. ETH Zurich)

presented by
EMILIE ZERMATTEN
Master of Science MSc en Physique, EPFL
born on 28.07.1985
citizen of St-Martin (VS)

accepted on the recommendation of
Prof. Dr. Aldo Steinfeld, examiner
Prof. Dr. Sophia Haussener, co-examiner
Dr. Martin Schneebeli, co-examiner

2013
Abstract

Tomography based direct pore-level simulations are applied to characterize porous media. The methodology used consists of obtaining the exact 3D geometry of porous media by the use of micro-computed tomography, which is used in discrete scale simulations for the determination of their effective heat and mass transfer properties. Morphological characteristics are obtained by two-point correlation function as well as morphology operations. Finite volume techniques are used to numerically solve the mass and momentum conservation equation to determine mass transport properties. Monte Carlo ray tracing allows for the acquisition of radiative properties.

The heat and mass transport properties of porous media are important for a wide range of applications. In particular, the application to snow, bone tissue engineering and solar thermochemical processes are of interest. In each of these fields, the study of the microstructure of the multiphase media is essential for the comprehension of natural phenomena or the improvement of a technical process. For this purpose, the determination of the effective transport properties of various porous media used in volume averaging models is crucial. This thesis is dealing with the determination of mass transport properties of snow, wall shear stress level in porous scaffold used for in-vitro bone formation and the radiative properties of a reticulated porous ceramic made of ceria, used in solar thermochemical processes.

Two different works are performed on snow, each with a particular sample set. The first study considers five samples, characteristics for a wide range of seasonal snow. Their 3D geometrical representations are obtained by micro-computed tomography and used in direct pore-level simulations to numerically solve the governing mass and momentum conservation equations. The second order extension to Darcy’s law is used to determine permeability and the Dupuit–Forchheimer coefficient. Simplified semi-empirical models of porous media are examined. The second set of snow consists of 34 samples, already characterized experimentally and casted with dimethyl phthalate. Sublimation tomography is performed to obtain their exact 3D geometry, which consists of scanning the cast to obtain the negative geometry of the snow sample. A combination of second and third order extensions of Darcy’s law is used to determine permeability, the Dupuit–Forchheimer coefficient and
the third order coefficient. Porosity and specific surface area are obtained by two-point correlation function. It is found that inertial effects, given by the second and third order correction in Darcy’s law, influence the air flow even at low Reynolds numbers. Correlations are derived for permeability, the Dupuit-Forchheimer coefficient and the third order coefficient of Darcy’s law as a function of density and grain size. Porosity, specific surface area and permeability are compared with the experimentally measured data on the exact same samples and yields good agreement. Tortuosity of each sample is determined. Anisotropy is observed in the tree coefficients of the extended Darcy’s law, and the anisotropy coefficients for permeability give a range consistent with the literature. The methodology presented allows for the determination of snow’s effective mass transport properties, which are strongly dependent on the snow microstructure and morphology and can be readily used in snowpack volume-averaged models. Two different extensions of Darcy’s law are used in these two studies, both equations presenting an accurate description of the increase of inertial effects with Reynolds number. Both studies emphasize the importance of the representative elementary volume, which size should not be underestimated for the acquisition of accurate results.

Furthermore, tomography based direct pore-level simulations are used in the field of medical engineering, with an application to bone tissue engineering. Two scaffolds used in a perfusion bioreactor for the in-vitro formation of bones are investigated. Their complex 3D geometries are imaged by micro-computed tomography and used in direct pore-level simulations of the entire scaffold-bioreactor system to numerically solve the governing mass and momentum conservation equations for fluid flow through porous media. The simulations are performed through the entire system comprising the scaffold inside the bioreactor. The velocity field and wall shear stress distribution are determined for both scaffolds. The more regular scaffold, made of polycaprolactone, exhibits an asymmetric distribution of wall shear stress with peak and plateau, while the silk fibroin scaffold, with an irregular microstructure, exhibits a homogeneous distribution and conditions the flow more efficiently than the polycaprolactone scaffold. The methodology guides the design and optimization of the scaffold geometry.

Finally, a reticulated porous ceramic made of cerium oxide designed for solar thermochemical processes is examined. Collision-based Monte-Carlo is used on its 3D geometry obtained by micro-computed tomography to determine its radiative properties. Distribution functions of attenuation path length and scattering angle are computed, yielding the extinction coefficient and scattering phase function. Spectroscopic measurements are carried out to validate the numerically determined extinction coefficient.

The presented methodology is shown to be applicable for various fields. The obtained effective properties can be directly incorporated in volume-
averaged models, such as snowpack models and models for the optimization of solar thermochemical reactors.
Résumené

Cette thèse présente la caractérisation de milieux poreux par l’application de simulations directes au niveau poreux basées sur la tomographie. La méthodologie consiste à obtenir la géométrie exacte en trois dimensions de matériaux poreux en utilisant la micro-tomographie assistée par ordinateur; cette géométrie est ensuite utilisée dans des simulations à échelle discrète pour la détermination de leurs propriétés effectives de transport de masse et de chaleur. Les caractéristiques morphologiques sont obtenues par une fonction de corrélation à deux points ainsi que par des opérations morphologiques. La technique des volumes finis est utilisée pour résoudre numériquement les équations de conservation de masse et de moment pour déterminer les propriétés de transport de masse. Le tracé de rayons de type Monte-Carlo permet l’acquisition des propriétés radiatives.

Les propriétés de transport de chaleur et de masse en milieux poreux sont importantes pour un large panel d’applications, parmi lesquelles l’application à la neige, à l’ingénierie du tissu osseux et aux procédés thermochimiques solaires. Dans chacun de ces domaines, l’étude de la microstructure des milieux multiphases est essentielle à la compréhension de phénomènes naturels ou à l’amélioration de procédés techniques. A cet effet, la détermination des propriétés de transport effectives de milieux poreux variés utilisées dans des modèles de moyenne volumique est cruciale. La présente thèse traite de la détermination des propriétés de transport de masse de la neige, du niveau de contrainte de cisaillement présente dans des supports poreux servant à la formation de tissu osseux in-vitro, et des propriétés radiatives d’une céramique poreuse réticulée faite d’oxyde de cérium, utilisée dans des procédés thermochimiques solaires.

Deux études différentes sont effectuées sur la neige, chacune sur une série d’échantillons distincte. La première étude prend cinq échantillons en considération, caractéristiques d’une large gamme de neige saisonnière. Leur représentation géométrique en trois dimensions est obtenue par microtomographie assistée par ordinateur et utilisée dans des simulations directes au niveau poreux pour résoudre numériquement les équations de conservation de masse et de moment. L’extension de second ordre à la loi de Darcy est utilisée pour déterminer la perméabilité et le coefficient de Dupuit-Fördchheimer. Des
modèles semi-empiriques de milieux poreux simplifiés sont examinés. La deuxième série consiste en 34 échantillons de neige, déjà caractérisés expérimentalement et moulés dans du phthalate de dyméthyle. La technique de tomographie par sublimation est utilisée pour obtenir leur exacte géométrie en trois dimensions. Cette méthode consiste à scanner le moulage afin d’obtenir la géométrie négative de l’échantillon de neige. Une combinaison de la deuxième et de la troisième extension de la loi de Darcy est utilisée pour déterminer leur perméabilité, leur coefficient de Dupuit-Forchheimer et le coefficient de troisième ordre de cette extension. La porosité et la surface spécifique sont obtenues par une fonction de corrélation à deux points. Il est observé que les effets d’inertie, donnés par les corrections de deuxième et de troisième ordre à la loi de Darcy, influencent l’écoulement de l’air déjà à un nombre de Reynolds bas. Des corrélations sont dérivées pour la perméabilité, le coefficient de Dupuit-Forchheimer et le coefficient de troisième ordre de l’extension de loi de Darcy en fonction de la densité et de la taille des grains. La porosité, la surface spécifique et la perméabilité sont comparées avec les données mesurées expérimentalement sur les mêmes échantillons et sont concordants. La tortuosité de chaque échantillon est déterminée. De l’anisotropie est observée pour les trois coefficients de la version corrigée de la loi de Darcy, et les coefficients d’anisotropie pour la perméabilité donnent des valeurs en accord avec la littérature. La méthodologie présentée permet la détermination des propriétés effectives de transport de masse de la neige, lesquelles sont fortement dépendantes de la microstructure et de la morphologie de cette dernière et peuvent être utilisées telles quelles dans des modèles de moyenne volumique du manteau neigeux. Deux extensions différentes de la loi de Darcy sont utilisées dans ces études, les deux présentant une description précise de l’augmentation de l’inertie avec le nombre de Reynolds. Ces deux études soulignent l’importance du volume élémentaire représentatif, dont la taille ne doit pas être sous-estimée pour l’acquisition de résultats précis.

De plus, les simulations basées sur la tomographie au niveau poreux sont utilisées dans le domaine de l’ingénierie médicale, plus particulièrement de l’ingénierie des tissus osseux. Deux matériaux de support utilisés dans un bioréacteur de perfusion pour la formation in-vitro de tissu osseux sont examinés. Leur géométrie complexe en trois dimensions est imagée par microtomographie assistée par ordinateur et utilisée dans des simulations directes au niveau poreux de l’entier du système support-bioréacteur afin de résoudre numériquement les équations de conservation de masse et de moment pour le flux de fluide en milieu poreux. Les simulations sont effectuées sur l’entier du système comprenant le support poreux et le bioréacteur l’entourant. Le champ de vitesses et les contraintes de cisaillement sont déterminés pour les deux supports. Le support le plus régulier, constitué de polycaprolactone, présente une distribution asymétrique des contraintes de cisaillement avec un
pic et un plateau, tandis que le support fait de fibroïne de soie, avec une structure irrégulière, présente une distribution homogène et conditionne le flux plus efficacement que le support de polycaprolactone. La méthodologie guide la conception et l'optimisation de la géométrie du support.

Finalement, une céramique poreuse réticulée faite d’oxyde de cérium conçue pour des procédés thermochimiques solaires est étudiée. La méthode de Monte-Carlo basée sur des collisions est utilisée sur sa géométrie en 3D obtenue par micro-tomographie assistée par ordinateur pour déterminer ses propriétés radiatives. Des fonctions de distribution de l'atténuation de la longueur du trajet et d'angle de diffusion sont calculées, afin d'obtenir le coefficient d'extinction et la fonction de phase de diffusion. Des mesures spectroscopiques sont effectuées pour valider le coefficient d'extinction déterminé numériquement.

Il est montré que la méthodologie présentée est applicable à des domaines variés. Les propriétés effectives obtenues peuvent être incorporées directement dans des modèles de moyenne volumique, tels que des modèles de manteau neigeux ou d'optimisation de réacteurs thermochimiques solaires.
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# Nomenclature

## Latin symbols

- \( A(K) \) anisotropy coefficient  
- \( A_0 \) specific surface area \([\text{m}^{-1}]\)  
- \( A, B, C \) constants in Equation (2.18)  
- \( d \) characteristic length scale \([\text{m}]\)  
- \( d_h \) hydraulic diameter \([\text{m}]\)  
- \( F \) Dupuit-Forchheimer coefficient \([\text{m}^{-1}]\)  
- \( F_s \) chord length probability distribution function  
- \( G_s \) cumulative chord length distribution function  
- \( I \) intensity \([\text{W} \cdot \text{m}^{-3} \cdot \text{sr}^{-1}]\)  
- \( K \) permeability \([\text{m}^2]\)  
- \( k_4, k_5 \) constants in Equation  
- \( l \) length \([\text{m}]\)  
- \( Kn \) Knudsen number  
- \( l_{\text{REV}} \) length of cubic REV \([\text{m}]\)  
- \( n \) normal unit vector  
- \( N \) number of rays  
- \( p \) pressure \([\text{N} \cdot \text{m}^{-2}]\)  
- \( q \) heat rate \([\text{W}]\)  
- \( r \) spatial location vector  
- \( r_e \) equivalent sphere radius of a grain  
- \( \text{Re} \) Reynolds number  
- \( s \) path length \([\text{m}]\)  
- \( \mathbf{s} \) unit directional vector  
- \( s_2 \) 2-point correlation function  
- \( u \) velocity \([\text{ml/min}]\)  
- \( u_D \) Darceean velocity (superficial volume-averaged velocity) \([\text{m} \cdot \text{s}^{-1}]\)  
- \( V \) volume \([\text{m}^3]\)  
- \( y \) height of the fluid above the phase boundary
Greek symbols

α  absorptivity
β  extinction coefficient [m⁻¹]
γ  third order coefficient in the extended Darcy’s law
δ  Dirac delta function
ε  porosity
θ  angle [°]
κ  absorption coefficient [m⁻¹]
λ  wavelength [m]
μ  dynamic viscosity [kg·m⁻¹·s⁻¹]
cosine of angle
Πpg  dimensionless pressure gradient
ρ  density [g·m⁻³]
σs  scattering coefficient [m⁻¹]
τ  tortuosity
τw  wall shear stress [Pa]
Φ  scattering phase function
ξ  half bandwidth for REV determination

Subscripts

Arakawa measured by Arakawa et al. [8]
DPLS simulated by DPLS
ex experimentally measured
i  counter
incident
num numerically calculated
op  opening
path fluid path
r emitted
radiative
refl reflected
s  scattered
sample sample
x  horizontal direction
z  vertical direction
0  initial

Abbreviations
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<tr>
<td>CAD</td>
<td>Computer Aided Design</td>
</tr>
<tr>
<td>CCD</td>
<td>charge coupled device</td>
</tr>
<tr>
<td>CFD</td>
<td>Computational Fluid Dynamics</td>
</tr>
<tr>
<td>CT</td>
<td>Computed Tomography</td>
</tr>
<tr>
<td>μ-CT</td>
<td>Micro Computed Tomography</td>
</tr>
<tr>
<td>DEP</td>
<td>Diethyl Phthalate</td>
</tr>
<tr>
<td>DF</td>
<td>Decomposing and Fragmented precipitation particles</td>
</tr>
<tr>
<td>DFdc</td>
<td>Partly decomposed precipitation particles</td>
</tr>
<tr>
<td>dh</td>
<td>depth hoar</td>
</tr>
<tr>
<td>DH</td>
<td>Depth Hoar</td>
</tr>
<tr>
<td>DHcp</td>
<td>Depth hoar, hollow cups</td>
</tr>
<tr>
<td>DMP</td>
<td>Dimethyl Phthalate</td>
</tr>
<tr>
<td>DPLS</td>
<td>Direct Pore Level Simulations</td>
</tr>
<tr>
<td>ds</td>
<td>decomposing snow</td>
</tr>
<tr>
<td>ECM</td>
<td>Extracellular Matrix</td>
</tr>
<tr>
<td>EMPA</td>
<td>Swiss Federal Laboratory for Material Science and Technology</td>
</tr>
<tr>
<td>FC</td>
<td>Faceted Crystals</td>
</tr>
<tr>
<td>FCsf</td>
<td>Near surface faceted particles</td>
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<tr>
<td>ICSSG</td>
<td>International Classification for Seasonal Snow on the Ground</td>
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<tr>
<td>IF</td>
<td>Ice Formations</td>
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<tr>
<td>MC</td>
<td>Monte Carlo</td>
</tr>
<tr>
<td>MF</td>
<td>Melt Forms</td>
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<tr>
<td>MFcl</td>
<td>Melt forms, clustered rounded grains</td>
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<tr>
<td>mI</td>
<td>metamorphosed snow I</td>
</tr>
<tr>
<td>mII</td>
<td>metamorphosed snow II</td>
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<tr>
<td>MM</td>
<td>Machine Made snow</td>
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<tr>
<td>NRMSE</td>
<td>Normalized Root Mean Square Error</td>
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<td>PCL</td>
<td>Polycaprolactone</td>
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<tr>
<td>PP</td>
<td>Precipitation Particles</td>
</tr>
<tr>
<td>PSI</td>
<td>Paul Scherrer Institute</td>
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<tr>
<td>REV</td>
<td>Representative Elementary Volume</td>
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<tr>
<td>RG</td>
<td>Rounded Grains</td>
</tr>
<tr>
<td>RGsr</td>
<td>Rounded Grains, small rounded particles</td>
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<tr>
<td>RMSE</td>
<td>Root Mean Square Error</td>
</tr>
<tr>
<td>ROI</td>
<td>Region Of Interest</td>
</tr>
<tr>
<td>RPC</td>
<td>Reticulate Porous Ceramic</td>
</tr>
<tr>
<td>SF</td>
<td>Silk Fibroin</td>
</tr>
<tr>
<td>SH</td>
<td>Surface Hoar</td>
</tr>
<tr>
<td>SSA</td>
<td>Specific Surface Area</td>
</tr>
<tr>
<td>Abbreviation</td>
<td>Description</td>
</tr>
<tr>
<td>-------------</td>
<td>--------------------------------------</td>
</tr>
<tr>
<td>TOMCAT</td>
<td>TOmographic Microscopy and Coherent rAdiology experimenTs</td>
</tr>
<tr>
<td>ws</td>
<td>wet snow</td>
</tr>
<tr>
<td>WSS</td>
<td>Wall Shear Stress</td>
</tr>
</tbody>
</table>
Chapter 1

Introduction

The determination of porous media’s transport properties has an interest for a wide range of applications. In chemical processes, porous materials are used for filtering, drying, catalytic packed bed reactors, fuel cells [88]; in an environmental and geological context, they are significant in the study of ground water flow, water flow through construction materials, waste disposal, irrigation, water percolation in snow, snow metamorphism, glaciological transport, geothermal energy [20,88]. In the mechanical field they can be applied for insulation, single- and two-phase transpiration cooling, combustion, nuclear reactors cooling, dehumidifying, solar energy storage, catalytic converters [88], metallurgy, cement production [134]; the petroleum industry makes a strong use of them to enhance the oil production, harvest oil and natural gas production [88]. Additionally, porous structures are used in biology, for tissue engineering [200], blood perfusion, skin barrier and the biomechanics of swelling [80].

The methodology presented in the next chapters has been originally developed for chemically-reacting, multi-phase media used in solar energy applications [66,134]. It uses micro-computed tomography (µCT) to obtain the exact 3D geometrical representation of a porous structure, before incorporating it in numerical models for the determination of morphological, heat and mass transport properties.

In this thesis, the extension to other fields, namely snow transport properties and bone tissue engineering, will be developed. The radiative properties of a ceria reticulated porous ceramic (RPC) will also be shortly analyzed.

1.1 Snow

Snow and ice play an essential role in the Earth’s climate system [47]. Snow covers on average approximately 47 million km$^2$, which corresponds to 9% of the Earth’s total surface [140,148]. In the northern hemisphere, it ranges from 3.8 million to 46.5 million km$^2$, depending on the season [154]. Antarctica
alone is covered by 14.5 million km² of snow [47]. Therefore, the amount of snow has a significant impact on climate and ecosystems [47], both globally and locally.

On a global scale, the snowcover influences the energy balance of the Earth’s surface [9]; its high albedo reduces the net radiation [155]. The albedo of fresh, dry snow ranges between 0.8 and 0.95, whereas the albedo of snow free vegetation or soil is only between 0.1 and 0.3 [9]. The thermal properties of snow affect the climate. Its thermal conductivity is around 0.1 W m⁻¹ K⁻¹; it is therefore a good insulator and allows deep water drainage to stay uninterrupted [9, 104]. Around 75% of the world’s terrestrial water reserves are contained in snow and ice [10]. In several semi-arid regions, runoff from mountain snowpack represents the major source of water [9]. As snow is permeable to gases, its large internal surface is subjected to interactions with atmospheric gases, with an impact on atmosphere chemistry [43]. Convection of air in snow can change the chemical composition of trapped atmospheric gases in ice-cores [168], with an implication in climatology and paleoclimatology: a good knowledge of the relation between snow and atmosphere allows for the reconstruction of past atmospheric chemistry with polar ice cores along several thousand years [96].

On a local scale, the snow cover influences regional weather [10, 107, 147]; its low conductivity makes it a good insulator for the ground and protects soil and vegetation from extreme temperatures [148]; it influences therefore the availability of nutrients and habitat [10, 117, 192]. The abundance or lack of snow also has more direct local effects. Winter tourism provides a high economic benefit in mountain regions such as Rocky Mountains, the Appalachians and the Alps [9]. However, the snowcover can induce additional costs, particularly in urban regions, by causing delays and accidents in transportation [9, 140]. Additionally, high snow cover can induce avalanches, which constitute a major natural hazard every winter [140]. Between 1985 and 2005, avalanches caused an average of 120 deaths per year in the Alps [9, 112]. In Winter 1998/1999, 17 persons perished in avalanches in Switzerland [167].

Snow is a sintered porous material made of ice grains, air, water vapor and sometimes liquid water [84]. Its complex porous microstructure consists of a continuous ice structure, made of grains connected by bonds, and continuously connected pores. The temperature of snow is always close to its melting temperature; it is therefore considered as a high temperature material: if we look at its homologous temperature (i.e. the absolute temperature divided by the absolute melting temperature of the material), snow is always found in nature at a very high homologous temperature, always above 0.85 [162]. Therefore, it continuously changes with time and external conditions due to rapid recrystallinization processes [162]; this process is called snow metamorphism. Snow crystals originally form in clouds; ice particles form on
impurities present in clouds (dust, salts) [148] and grow by diffusion of water vapour (deposition), collision with supercooled drops (riming) and collision with other snow crystals (clumping or aggregation) [145]. Snowflakes exhibit a large range of different morphologies; the temperature, the humidity and the degree of supersaturation of water vapor influence their shape [9,99,148]. After forming, the snowflakes will fall on the ground and create a snow layer; the crystals will sinter into a porous structure. The different shapes of the crystals themselves, in addition to the metamorphism they are subjected to once on the ground, leads to a broad range of different snow structures [148]. There have been several attempts to classify them over the years.

The most up-to-date classification is the *International Classification for Seasonal Snow on the Ground* (ICSSG) [50]. It classifies the snow by several characteristics. The primary physical characteristics of deposited snow are its microstructure, grain shape, grain size, snow density, snow hardness, liquid water content, snow temperature, impurities and layer thickness [50]. The main grain shape classes are described in Table 1.1. Each of them is divided into several subclasses. Figure 1.1, 1.2, 1.3 and 1.4 show examples of the various grain shapes found in nature.

<table>
<thead>
<tr>
<th>Class</th>
<th>Symbol</th>
<th>Code</th>
</tr>
</thead>
<tbody>
<tr>
<td>Precipitation Particles</td>
<td>+</td>
<td>PP</td>
</tr>
<tr>
<td>Machine Made snow</td>
<td>⊙</td>
<td>MM</td>
</tr>
<tr>
<td>Decomposing and Fragmented precipitation particles</td>
<td>/</td>
<td>DF</td>
</tr>
<tr>
<td>Rounded Grains</td>
<td>●</td>
<td>RG</td>
</tr>
<tr>
<td>Faceted Crystals</td>
<td>□</td>
<td>FC</td>
</tr>
<tr>
<td>Depth Hoar</td>
<td>∧</td>
<td>DH</td>
</tr>
<tr>
<td>Surface Hoar</td>
<td>∨</td>
<td>SH</td>
</tr>
<tr>
<td>Melt Forms</td>
<td>○</td>
<td>MF</td>
</tr>
<tr>
<td>Ice Formations</td>
<td>■</td>
<td>IF</td>
</tr>
</tbody>
</table>

Snow porosity can range between 0.9 and 0.2 [162], its grain size can be smaller than 0.2 mm and bigger than 5 mm [50]. Amongst others, these large differences lead to a wide range of properties of snow. Its morphological characteristics, such as porosity or density, are not sufficient to characterize its heat and mass transport properties; they are strongly influenced by the microstructure. Therefore, it is essential to find accurate methods to determine these properties. In this thesis, the determination of permeability in snow will be emphasized. Snow permeability has a direct effect on the snow-air exchange processes relevant to the composition of the lower atmosphere [34,63], on snow metamorphism [4,127] and on water flow through
CHAPTER 1. INTRODUCTION

Figure 1.1: Partly decomposed precipitation particles (DFdc): These particles still show the characteristics of precipitation particles, but are partly rounded. They form within the snowpack and are recently deposited near the snow surface, usually dry [50].

Figure 1.2: Depth hoar, hollow cups (DHcp): The particles are striated, usually cup-shaped. They form within the snowpack and are dry rounded. They form within the snow surface, usually dry [50].

Figure 1.3: Near surface faceted particles (FCsf): The particles are faceted crystals in surface layer. They form right beneath the surface large ice-to-ice bonds; they contain water in internal veins. They form at the surface or within the snowpack and are dry snow water [50].

Figure 1.4: Melt forms, clustered rounded grains (MFcl): They form a cluster of rounded crystals held by large ice-to-ice bonds; they contain water in internal veins. They form at the surface or within the snowpack and are wet snow [50].
1.2. BONE TISSUE ENGINEERING

Bone is a complex material made of collagen fibers, a calcium phosphate matrix and living bone cells. It is known to react to biomechanical forces. A change in function of a bone leads to alterations in bone architecture and bone mechanical strength [212]. Living bone continuously grows and adapts to the demands of the mechanical environment through a mechanism called bone remodeling. Three different cell types participate in bone remodeling: i) osteoblasts, ii) osteocytes, and iii) osteoclasts. Osteoblasts are the bone forming cells that deposit new organic and inorganic matrix. Osteocytes are considered the mechanoreceptors in bone [1,5,28], and osteoclasts are responsible for bone degradation [190]. External forces acting on the bone create tension and pressure sites inside the bone’s lacunocanalicular network. This pressure gradient leads the interstitial fluid to flow through the canalicular network. Osteocytes sense fluid shear stresses [5] and compile this information into a signal cascade to activate or inhibit bone-forming osteoblasts and bone-resorbing osteoclasts.

As the world population is progressively aging, medicine is constantly facing new challenges. One of them is the increase of bone diseases. For example, osteoporosis results in a loss of bone mass and the deterioration of bone tissue [18,132], which increases the risk of fractures and makes their healing
more difficult. Only in the United States, the fractures due to osteoporosis are estimated to 1.5 million each year; this number is expected to increase with the aging of the population [153]. Several other diseases can affect bones as well as cartilage: arthrosis, rheumatoid arthritis, osteoarthritis, congenital malformation [115], osteogenesis imperfecta or osteomyelitis [144]. Injuries, such as orthopedic surgeries and primary tumor resection induce bone defects as well [144]. Bone repair often results in a non-union, i.e. the bone is not able to repair itself; if the bone loss is too large, it will not be healed by fixation [144]. For those scenarios, several treatments are possible: the standard one is autogeneous bone grafting. It consists in filling the defect with a bone removed from another part of the body [144]. However, this can lead to donor site morbidity and pain, and induce additional surgery [94, 190]. An alternative treatment is allograft, i.e. the implant of bone tissue from other humans, which has already been applied successfully. However, it has shown risks of infection, host immune response and shortage of tissue availability [94,130,144,190]. Xenografts (i.e. the use of non-human tissue) shows even more disadvantages (disease, infection, toxicity associated with sterilization, immune response) and are unsuitable [94, 144, 214]. The drawbacks of these methods motivate the research in bone tissue engineering.

Tissue engineering is the application of engineering principles to life sciences in order to restore, maintain or improve functions of the living organism [125]. It consists in the use of a porous artificial 3D scaffold to provide a support for bone-in-growth and guide extra-cellular matrix (ECM) production. There are two different approaches in bone tissue engineering: i) implantation of a scaffold alone directly into the bone, and ii) isolation of mesenchymal stem cells in vitro, which are seeded into a scaffold to produce ECM, before implanting it in the defect bone [144]. This latter approach is used in this thesis. Tissue engineering provides the advantages of eliminating the risk of disease transmission, a reduced risk of immune response and the diminution of surgical procedures [144]. However, the current approaches are limited with regard to being able to restore both the complexity of most tissues and the potential of up-scaling such in vitro grown constructs to clinically relevant sizes. A potential approach to decipher the complexity of tissue engineering problems is the bottom-up approach [128]. The bottom-up approach investigates a system from small scales like atoms, molecules or cells, towards larger scales like cell aggregates, various tissue components and finally the full functional tissue. Tissue engineering studies performed according to the bottom-up approach help to understand how tissue building blocks interact with each other, which leads to a better understanding of the whole living system. Additionally, these studies provide tissue engineers more guidance on the cellular scale to direct the development at a large tissue scale and enable controlled interventions rather than the present observatory studies.
The three main components that constitute a tissue engineering culture are i) living cells, ii) a three-dimensional (3D) scaffold and iii) the physico-chemical culture environment. The ultimate goal should be to predict how various interventions affect the behavior of a cell-scaffold construct both in vitro and later on even after implantation in vivo. Such a forward-controlled approach becomes even more essential when artificial matrices such as porous 3D scaffolds are applied as temporal supportive structures, as they considerably change the environment of the cells away from what they naturally feel [141].

The first attempts to develop cells in a scaffold in vitro used static cultures, with cells seeded onto scaffolds and placed into well plates [77, 174, 200]. However, with these culture conditions, cells have shown to grow preferentially at the periphery of the scaffold [61], leading to the necrosis of the center due to poor nutrient exchange [200]. To overcome these drawbacks, dynamic bioreactors have been developed; they enable loading of the construct [53, 207]. Several types of dynamic bioreactors mimicking the various tissue conditions have been developed so far [200]: i) rotating wall vessel bioreactors [166], ii) spinner flask bioreactors [53], iii) compression bioreactors [11] and iv) perfusion bioreactors [15]. The advantages of dynamic bioreactor cultures over static cultures have been shown in several studies [27, 41, 172]. The perfusion bioreactor is thought to mimic the loading conditions of osteocytes within the canalicular network in vitro most closely. Flow perfusion has been shown to increase cell number, improve the distribution of cells and the amount of deposited (mineralized) ECM on the scaffold as well as an enhanced expression of the osteogenic phenotype [16, 27, 41, 62, 172, 173]. In tissue engineering studies with flow perfusion bioreactors, mechanical input is usually generated through the adaptation of the flow rate at the pump connected to the system. However, a set flow rate at the pump does not directly reflect the flow rate within a porous scaffold or the shear stress that a cell attached to the scaffold surface encounters. The geometry of the reactor and of the scaffold, as well as the scaffold material, have a great influence too.

Scaffold properties play an important role in perfusion cultures. Several materials are currently used to elaborate them: tissue derived materials (e.g. allograft bone matrix, skin), biological polymers (e.g. collagen, silk fibroin, alginate), ceramics and mineral based foams (e.g. hydroxyapatite, calcium sulphate), metals and composites of two or more materials [123, 190]. Synthetic polymers have recently been developed [123]. Scaffold microstructure has direct influence on the cellular behavior and the mechanical stimuli cells feel. Pore interconnectivity promote space for tissue formation, vascularization and offers pathways for mass transport [123, 190]. Pore size and porosity directly influences cell behavior [26, 87, 190, 201, 215]. To mimic healthy or diseased shear stresses in an in vitro model of healthy or diseased bone with
a perfusion bioreactor, it is important to know the mechanical stimuli a cell experiences at a given flow rate in a certain location in the 3D volume of a scaffold.

Simulations are already widely used in bone tissue engineering to predict the mechanical environment in bioreactor systems [29, 33, 61, 106]. Perfusion systems have been already studied thoroughly using mechanical models like the cylindrical pore model (CPM). The CPM however, is a very simple model, not representing the real irregular, 3D structure of most scaffolds. It approximates the scaffold as a cylinder with cylindrical holes and was mostly used to estimate shear stresses at different flow velocities, but not to define shear stresses at distinct points in the real scaffold geometry [61, 64]. Finite element models can predict the biophysical stimuli in biological tissues more precisely [25]. Computational fluid dynamics (CFD) simulations are especially suitable to predict shear stresses acting on cells as well as fluid velocities and fluid pressure in scaffolds [106]. CFD simulations are widely used in combination with micro-computed tomography (µCT) scans of scaffolds to define the physical boundary conditions of the simulation [33, 106, 143, 205]. In this thesis, direct pore level simulations (DPLS) are applied on µCT 3D morphological representations of scaffolds used in bone tissue engineering for the determination of the shear stress acting on their interface.

1.3 Ceria RPC

Energy supply is one of the most important challenges of the 21st century. The need for fuels is constantly increasing, especially with the growing needs of the emerging countries. In 2011, the energy world consumption was mostly supplied by oil (31.5%), coal (28.8 %) and gas (21.3%) [81]. Therefore, a shift towards a more sustainable fuel supply is essential to reduce the global CO₂ emissions. Amongst the different renewable energy resources available, solar energy is the most abundant one, being available in large excess. Covering only 0.1 % of the Earth’s land space with solar collectors with an efficiency of 20% would be sufficient to cover the annual energy needs of the planet [187]. However, solar energy has disadvantages: the solar radiation is very dilute, intermittent and unequally distributed over the surface of the Earth [187]. To overcome these drawbacks, solar concentration and conversion to an energy form that could be stored long term and transported long range are essential.

To concentrate solar radiation, the main optical systems used are trough, tower and dish systems [187]. These systems can typically attain a solar flux concentration ratio of the order of 100, 1000 and 10,000 suns, respectively [183]. There are three ways to produce fuels from solar energy: electrochemical, photochemical, and thermochemical [183, 186]. Here, the thermochemical production of hydrogen will be discussed. It could be achieved
by direct water splitting, called water thermolysis:

$$H_2O \rightarrow H_2 + 0.5O_2 \quad (1.1)$$

However, this simple process shows several drawbacks. To achieve enough
dissociation, the process needs a temperature above 2500 K. Moreover, the
reaction leads to an explosive mixture which needs to be separated to prevent
recombination [183]. To overcome these problems, a two-step cycle using
oxide redox reactions is proposed [6,57,183–185]:

First step: $M_xO_y \rightarrow xM + \frac{y}{2}O_2 \quad (1.2)$

Second step: $xM + yH_2O \rightarrow M_xO_y + yH_2 \quad (1.3)$

in which M is a metal and $M_xO_y$ its corresponding metal oxide. For the
second step, CO$_2$ or a mixture of CO$_2$ and H$_2$O can be used:

$$xM + yCO_2 \rightarrow M_xO_y + yCO \quad (1.4)$$

This process would lead to a mixture of H$_2$ and CO, called synthesis gas,
or syngas, which can be used to produce synthetic fuels, such as Fischer–
Tropsch type chemicals, hydrogen, ammonia, and methanol [186]. The metal
oxide resulting from the second step can be reused in the first step. Several
water/H$_2$O-splitting thermochemical cycles using metal oxides have been used
experimentally, such as zinc oxide, iron oxide, cerium oxide and tin oxide [180].
Capturing CO$_2$ from air [58,129,213] to use it in the reactions (1.2), (1.3) and
(1.4) would produce carbon neutral fuels.

These processes are performed in a solar reactor, in which the metal oxide
is generally introduced in the form of a two-phase medium, such as porous
ceramics [74,92], packed beds [181,210] or fluidized beds [60,202,203]. Their
morphology will strongly influence the heat diffusion provided by the concen-
trated solar radiation, as well as the transport of the reactants. The compre-
hensive study of their heat and mass transfer properties is therefore essential
for the improvement of the process. Since the processes relevant to the porous
medium are in the order of a micrometer, and the reactor is in the order of
a meter, the modeling of both parts at the same time would be impossible.
Therefore, the volume-averaging method is used. Basically, the conservation
equations that are valid in the separate phases are developed to yield equa-
tions valid throughout the multi-phase medium [88,209]. The properties of
the porous medium are determined by solving the conservation equations in
the fluid phase, and can then be applied on the averaged porous media to
model it in a larger scale. The geometry of the porous media can be obtained
by the use of tomography, to determine its properties by numerical methods.
1.4 Thesis outline

In this thesis, tomography based direct pore level simulations (DPCLS) are used for the characterization of porous media. The methodology that was previously developed for multi-phase media used in solar and solar-thermo-chemical applications is extended to the application to snow and bone tissue engineering.

In Chapter 2, definitions and the methodologies used to characterize porous media are given. The technique of micro-computed tomography is explained. The methodology to determine the representative elementary volume, porosity, specific surface area, pore and particle size and tortuosity are given. The different extensions of Darcy’s law are provided. Fundamentals of radiation in participating media and Monte Carlo method are stated.

Chapter 3 is dedicated to the determination of snow properties. Two studies on different samples are presented. The first set of samples is composed of five different snow types, characteristic for a wide range of seasonal snow. Their 3D geometrical representations are obtained by µCT and used in direct pore-level simulations to numerically solve the governing mass and momentum conservation equations, allowing for the determination of their effective permeability and Dupuit–Forchheimer coefficient. Simplified semi-empirical models of porous media are also examined. The methodology presented allows for the determination of snow’s effective mass transport properties, which are strongly dependent on the snow microstructure and morphology and can, in turn, readily be used in snowpack volume-averaged (continuum) models such as strongly layered samples with macroscopically anisotropic properties. This study provides a first insight into the use of DPLS for the characterization of snow.

The second set of samples consists of 34 samples which were already characterized experimentally in a previous study. Sublimation tomography is used to determine their specific surface area, porosity, effective permeability, anisotropy, and tortuosity. Their 3D geometrical representation is used in direct pore-level simulations (DPLS) to numerically solve the governing mass and momentum conservation equations for fluid flow through porous media. It is found that inertial effects, given by a second and third order correction in Darcy’s law, influence the air flow even at low Reynolds numbers. Correlations are derived for permeability, the Dupuit-Forchheimer coefficient and the third order coefficient of Darcy’s law as a function of density and grain size. Comparison with the experimentally measured data yields good agreement and confirms the applicability of DPLS for the determination of transport properties of snow.

Chapter 4 is dedicated to bone tissue engineering. The study presented takes two basic constituents of a tissue culture as well as how they are influ-
enced by each other into account: 3D scaffolds and a controlled mechanical environment in a dynamic flow perfusion bioreactor. Two 3D scaffold types, exemplified here with two commonly used scaffold materials and geometries, are investigated. The aim of this study is to determine the magnitude of wall shear stress (WSS) acting on cells seeded on a surface of two types of porous 3D scaffolds in a perfusion bioreactor. The cellular mechanical environment is studied with the help of µCT based numerical simulations of the scaffold in combination with the bioreactor environment. Additionally, the level of WSS for each potential cell location on the scaffold is calculated. Fluid flow through the scaffold placed in a perfusion bioreactor is simulated by DPLS. The velocity field and wall shear stress distribution are determined for both scaffolds. The methodology guides the design and optimization of the scaffold geometry.

Chapter 5 is dedicated to the determination of the radiative properties of a ceria reticulated porous ceramic used in a solar thermochemical cycle based on redox reactions. A 3D digital representation of the RPC is obtained by µCT and used in a collision-based Monte Carlo (MC) method to determine its extinction coefficient and scattering phase function. Spectroscopy measurements are carried out to validate the numerically determined extinction coefficient.
Chapter 2
Methodology

2.1 Computed tomography

Computed tomography (CT) is a non-destructive technique to produce three-dimensional representations of an object by combining 2D projections to reconstruct its exact structure. A large number of rays is passed through the object, and the modification of the rays caused by their interaction with the sample material is measured [17]. Different modes can be applied; the absorption mode gives a contrast by the difference between the attenuation coefficients [158], the phase contrast by the refractive index, and the diffraction mode by the scattering coefficient [66, 73]. The most widely used CT technique is the X-ray CT, in which the data is obtained by measuring the attenuation of X-rays through the cross sections of the sample [73]. Other CT techniques include positron emission tomography, based on radiation emitted by a living body [14, 86, 122], electrical impedance or resistance tomography, in which an image of the conductivity or permittivity of a conducting object is derived from surface electrical measurements [17, 142], atom probe tomography, providing an atomic resolution [17], proton tomography [82], electron tomography [19, 93], neutron tomography [204], ultrasound tomography [59] and radio tomography [146], amongst others.

In this thesis, X-ray tomography was used, which can use two-types of X-ray sources [66]: micro focus X-ray tube, which are widely applied for medical applications, and synchrotron radiation [182]. In the case of micro focus X-ray tube, a polychromatic, divergent beam is generated with a given solid angle; the detector can be either a 1D line detector or a 2D charge coupled device (CCD) camera; the sample is placed between the source and the detector [158]. The resolution of this type of tomography can vary between 10 and 500 µm. Synchrotron radiation tomography uses a very high flux at a small source size; a parallel monochromatic beam is used, and the detector is usually a CCD based detector [158, 182]. The resolution lies typically between 0.09 and 2.8 µm for the Swiss Light Source TOMCAT at Paul Scherrer Institute (PSI) [182].
The image is represented by voxels, a volume element corresponding to a 3D pixel.

2.2 Image processing

CT yields data in the form of gray levels representations of the X-ray extinction coefficient, arranged in a 3D matrix. Each voxel has a gray value, generally between 0 and 255 in the case of 8 bit integers, or between 0 and 65535 in the case of 16 bit. The images obtained are generally enhanced by image processing. The noise is typically reduced by applying a smoothing filter, such as a Gauss or Box filter. However, this technique can affect the sharp edges present on the image [85]. To reduce the noise and preserve the edges of the structure, other filters can be applied, such as non-linear diffusion filter, shock filter, inverse scale space filter or an anisotropic diffusion filter followed by an unsharp mask filter [85,169].

To characterize a porous medium, which is generally represented by two phases (solid and void), its tomographic data has to be separated into these two different phases. This is done by segmentation, by assigning each voxel into one phase [66]. The histogram of the gray values of a porous medium shows generally two distinct maxima, each of them representing one phase. The mode method separates the gray values by choosing the minimum between the two maxima as the threshold [208] representing the solid-void interface. Other segmentation methods have been described in [208]. Figure 2.1 shows the tomography data of a porous medium (snow in this case) being segmented between solid and void phase.

2.3 Mesh generation

To perform fluid dynamic simulations with a finite-volume method, the geometry of the porous media has to be represented by a mesh. An in-house mesh generator [55] is used to create a computational grid directly from the segmented tomography data. The mesh generator first covers the entire domain with tetrahedrons, which are then gradually divided into smaller tetrahedrons according to a refinement process which will split a tetrahedron if it is crossing a phase boundary. After several refinement processes, mesh consistency is established by splitting some of the cells. To fit the mesh surfaces to the surface of the geometry, vertices located close to a surface-crossing edge are moved to the closest surface point; this procedure is called vertex rounding. The remaining surface-crossing tetrahedra are cut into smaller polyhedra. The final step is a smoothing procedure, in which the mesh quality is improved by fine adjustments of node positions.
2.4 REPRESENTATIVE ELEMENTARY VOLUME

The representative elementary volume (REV) is defined as the minimum volume of a porous material for which the continuum assumption is valid [67]. It is determined by calculating a certain property $x$ of a medium for subsequently growing volumes, until it asymptotically reaches a constant value within a band of $\pm \xi$. The edge length of a cubic REV, $l_{REV}$, for a certain property $x$ and within a band of $\pm \xi$ is defined as:

$$l_{REV,\xi}(x) = \min\{l \leq l^* | x - \xi < x(V_l) < x + \xi\}, \quad (2.1)$$

where $V_l$ is a sample subvolume of edge length $l^*$. Note that the REV depends on the property for which it is calculated, e.g. the calculations based on pressure drop give larger REVs than the ones based on porosity [67,217].
2.5 Porosity

Porosity, $\varepsilon$, is defined as the fraction of volume occupied by pore space, i.e. the total void volume divided by the total volume occupied by solid and void [45, 88].

$$\varepsilon = \frac{V_v}{V_v + V_s},$$  \hspace{1cm} (2.2)

with $V_v$ the void volume and $V_s$ the solid volume. Effective porosity is the volume fraction of the interconnected pores [88]. Porosity can be calculated simply by counting each black and white voxels for the case of segmented data, or by comparing each voxel with the threshold for a non-segmented data. It can also be computed by two-point correlation function, which will be defined in section 2.7.

2.6 Specific surface area

Specific surface area (SSA), $A_0$, is defined as the interstitial surface area of the pores per unit mass or per unit volume [45]. In this thesis, SSA will always be defined as the pore area divided by the total volume, i.e.:

$$A_0 = \frac{A}{V_v + V_s},$$  \hspace{1cm} (2.3)

with $A$ the interstitial area. However, one has to be careful with this definition, since some studies might define it as the pore area divided only by the solid volume ($A_0 = \frac{A}{V_s}$), especially in the snow field [8]. SSA can be calculated either by voxels, or by two-point correlation function (see Section 2.7)

2.7 Two-point correlation function

The two-point correlation function is defined as the probability of two arbitrary points at a distance $r$ to be in the void phase [22]:

$$s_2(r) = \frac{\int_V \int_{4\pi} \Psi(x)\Psi(x + r\hat{s})d\hat{s}dx}{V4\pi}. \hspace{1cm} (2.4)$$

With the following properties:

$$s_2(r = 0) = \varepsilon$$  \hspace{1cm} (2.5)

$$s_2(r \to \infty) = \varepsilon^2$$  \hspace{1cm} (2.6)
\[ \frac{ds}{dr} \bigg|_{r=0} = -\frac{A_0}{4} \] (2.7)

which can be therefore used to determine porosity and specific surface area.

## 2.8 Pore and particle size

The pore size in porous media has been defined by various ways. A commonly used definition is the hydraulic diameter \( d_h \), defined as [88]:

\[ d_h = \frac{4\varepsilon}{A_0}. \] (2.8)

Other definitions have been proposed, based on chord-length distribution or area distributions of intersected pores [134,191]. Here, the pore size is defined as the diameter of a sphere which fits completely in the pore space, and similarly for the particle size. To determine them, the principle of granulometry is applied [176]; for a granular material, it consists of sieving a sample through sieves of increasing mesh size and measure the mass retained at each step. This way, a size distribution of the granules can be established. This concept can be applied similarly with mathematical morphology. An opening is applied on the 3D image of the structure, which consist of an erosion with a structuring element followed by a dilation with the same element. For a spherical structuring element with diameter \( d \), the distribution function is defined by [66]:

\[ f(d) = -\frac{d\varepsilon_{op}(d)}{\varepsilon dd}, \] (2.9)

with \( \varepsilon_{op} \) the porosity obtained after the opening.

## 2.9 Navier-Stokes

The mass and momentum conservation equations are solved with a commercial finite-volume method [7]:

\[ \frac{\partial \rho}{\partial t} + \nabla \cdot (\rho \mathbf{u}) = 0 \] (2.10)

\[ \rho \left( \frac{\partial \mathbf{u}}{\partial t} + \mathbf{u} \cdot \nabla \mathbf{u} \right) = -\nabla p + \mu \Delta \mathbf{u}, \] (2.11)

where \( \rho \) is the density of the fluid, \( \mathbf{u} \) the velocity, and \( \mu \) is the dynamic viscosity.
2.10 Tortuosity

Tortuosity is defined as the ratio of the path through the connected pore channels to the thickness of the porous sample in the main flow direction [66]:

$$\tau = \frac{l_{\text{path}}}{l_{\text{sample}}}.$$  \hspace{1cm} (2.12)

It is calculated by generating streamlines through the sample and averaging their length. The value of \(\tau\) is not constant and depends on the velocity of the flow through the porous media [88].

2.11 Wall shear stress

The wall shear stress is defined as:

$$\tau_w = \mu \frac{\partial u}{\partial y}|_{y=0},$$  \hspace{1cm} (2.13)

where \(y\) the height of the fluid above the phase boundary.

2.12 Darcy’s law and its extensions

At low fluid velocities, the pressure drop over a spatially averaged isotropic porous medium is given by Darcy’s law [40]:

$$\nabla p = -\frac{\mu}{K} u_D,$$  \hspace{1cm} (2.14)

where \(p\) is the pressure, \(K\) is the permeability, \(\mu\) is the dynamic viscosity of the fluid and \(u_D\) its superficial velocity, with volume \(V\) larger or equal to REV. However, this equation remains true only at very low Reynolds number \(\text{Re} (\text{Re} \rightarrow 0)\). At higher fluid velocities, equation (2.14) gets separated into two different regimes [95, 175, 179].

\textbf{Weak inertia} takes place when \(\text{Re} = O(\delta^{1/2})\), where \(\delta\) is the small scale separation parameter, \(\delta = d/L\). \(d\) is a characteristic length scale of the pores and \(L\) is a characteristic length of the macroscopic flow. At the weak inertia regime, the correction to Darcy’s law is a cubic term in velocity given by:

$$\nabla p = -\frac{\mu}{K} u_D - \frac{\gamma \rho^2}{\mu} u_D^3,$$  \hspace{1cm} (2.15)

where \(\rho\) is the fluid density and \(\gamma\) is a dimensionless factor.
Strong inertia starts at $\text{Re} = O(1)$ and is described by the Dupuit-Forchheimer equation [46,51]:

$$\nabla p = -\frac{\mu}{K} u_D - F \rho u_D^2,$$  

(2.16)

where $F$ is the Dupuit-Forchheimer coefficient.

Since determination of the transitional $\text{Re}$ between weak and strong inertia is difficult, a global equation to describe all the laminar regimes at once is used [156]:

$$\nabla p = -\frac{\mu}{K} u_D - F \rho u_D^2 - \frac{\gamma \rho^2}{\mu} u_D^3.$$  

(2.17)

The first term is the result of viscous effects, predominant at low velocities, whereas the second and third terms describe the inertial effects, which become important at higher fluid velocities. Note that these deviations do not come from turbulence [95, 156, 175]; these equations are describing laminar flows. Non-dimensionalization of eq. (2.17) yields the normalized pressure drop $\Pi_{pg}$:

$$\frac{\nabla pd^2}{\mu u_D} = \Pi_{pg} = \frac{d^2}{K} + Fd\text{Re} + \gamma \text{Re}^2 = A + B\text{Re} + C\text{Re}^2,$$  

(2.18)

where $d$ is a characteristic length scale, and $A$, $B$ and $C$ are constants. Some studies [67,71,136] neglect the weak inertia regimes and use Eq. 2.16 to describe all the laminar regimes. Non-dimensionalization of Eq. 2.16 yields:

$$\frac{\nabla pd^2}{\mu u_D} = \Pi_{pg} = \frac{d^2}{K} + Fd\text{Re} = A + B\text{Re}.$$  

(2.19)

In this thesis, both Equations (2.18) and (2.19) will be used. Although slightly less precise, Equation (2.19) yields an accurate fit to calculated data, and therefore describes well the change of pressure drop with increasing inertial effects.

### 2.13 Radiative properties

#### 2.13.1 Fundamentals of radiation in participating media

The study of the radiative properties is based on the fundamentals of continuum treatment of radiation on participating media [118,134,171]. The radiative transfer equation (RTE) inside a participating medium is given by:
\[
\frac{dI_\lambda}{ds} = \hat{s} \cdot \nabla I_\lambda = \kappa_\lambda I_{\lambda b} + \beta_\lambda I_\lambda + \frac{\sigma_{s\lambda}}{4\pi} \int_{4\pi} I_\lambda(\hat{s}_i) \Phi(\hat{s}_i, \hat{s}) d\hat{s}_i. \tag{2.20}
\]

Where \(I_\lambda\) is the radiative energy flux per unit solid angle and wavelength. The first term on the RHS denotes the augmentation by emission, where \(I_{\lambda b}\) is the black-body intensity for the medium temperature at a given location and \(\kappa_\lambda\) the absorption coefficient. The second term expresses the reduction by extinction, where \(\beta_\lambda\) is the extinction coefficient. The third term on the RHS gives the augmentation by in-scattering, where \(\Phi(\hat{s}_i, \hat{s})\) is the phase function, i.e. the probability that a ray is scattered from direction \(\hat{s}_i\) into \(\hat{s}\).

The spectral radiative heat flux vector is given by:
\[
\mathbf{q}_{r,\lambda} = \int_{4\pi} I_\lambda(\hat{s}) d\hat{s}. \tag{2.21}
\]

With its divergence, which gives the amount of energy stored per differential volume element and per unit wavelength:
\[
\nabla \cdot \mathbf{q}_{r,\lambda} = \kappa_\lambda \left( 4\pi I_{\lambda b} - \int_{4\pi} I_\lambda d\hat{s} \right). \tag{2.22}
\]

By integrating over all wavelengths, one obtains:
\[
\nabla \cdot \mathbf{q}_r = \int_0^\infty \kappa_\lambda \left( 4\pi I_{\lambda b} - \int_{4\pi} I_\lambda d\hat{s} \right) d\lambda. \tag{2.23}
\]

### 2.13.2 Monte Carlo method

A Monte Carlo (MC) method for the numerical determination of radiative properties of porous media has been developed previously [66–71, 100, 101, 134, 135, 137, 189]. It allows the determination of the extinction coefficient \(\beta\), the absorption coefficient \(\kappa\), the scattering coefficient \(\sigma_s\) and the phase function \(\Phi\) from the exact 3D geometry of a porous medium, obtained by computer tomography. To apply the MC method, the following assumptions are made:

- the medium is statistically homogeneous and isotropic;
- diffraction is neglected;
- geometrical optics apply;
- solids are opaque;
- the gas phase is non-participating (i.e. transparent: \(\kappa_{\text{gas}} = \sigma_{\text{gas}} = 0\)).
The MC method is carried out by launching a large number of rays \( N_r \) within the void phase of a volume \( V_0 \). This volume must be bigger than the smallest REV, but significantly smaller than the linear dimension of the participating medium. The \( N_r \) rays are emitted isotropically along random directions \( \hat{s} \) from uniformly distributed points \( r_0 \). Each ray is traced to its first intersection with the void/solid interphase to measure the path-length between emission and collision \( s = |r_0 - r_i| \) by following it in discrete steps \( \Delta s \). At each iteration, the following expression is evaluated for the gray value: 
\[
\Psi(r_0 + s\hat{s}) - \Psi_0, \text{ with } s = s + \Delta s.
\]
Bisection method is applied to determine the location of the phase boundary. Either absorption or reflection occurs at point \( r_i \). The direction \( \hat{s}_s \) for the scattered ray can be determined for two cases: diffuse reflection (where \( \hat{s}_s \) goes to a random direction in the normal hemisphere of the interphase) and specular reflection (where \( \hat{s}_s \) is determined by Fresnel Equations). The cosine of the incident angle \( \theta_i \) is computed by  
\[
\mu_i = \cos \theta_i = -\hat{s} \cdot \hat{n}_i.
\]

The probabilistic chord length distribution of the path-lengths \( s_j \) can be expressed as:
\[
F_s(s) = \frac{1}{N_r} \sum_{j=1}^{N_r} \delta(s - s_j) \tag{2.24}
\]
where \( \delta \) is the Dirac Delta function. The integration of this term leads to the cumulative chord length distribution function:
\[
G_s(s) = \int_0^s F_s(s') ds' \tag{2.25}
\]
which describes the radiation intensity decline of an unextincted bundle of rays through the porous medium as following:
\[
\frac{I(s)}{I_0} = 1 - G_s(s) \tag{2.26}
\]
and can be compared to Bouguer’s law in the participating media approach for a constant extinction coefficient \( \beta \):
\[
\frac{I(s)}{I_0} = e^{-\beta s} \tag{2.27}
\]

A fit to Equation 2.27 with the computed results obtained for Equation 2.26 allows the determination of \( \beta \).

According to the opaque solid phase assumption, the scattering albedo \( \sigma_s/\beta \) equals the reflectivity of the solid surface. Only purely diffuse or perfectly specular surfaces with directional-hemispherical reflectivity are here
considered. The scattering coefficient is then given as:

$$\sigma_s = \rho \beta = (1 - \alpha) \beta$$

(2.28)

and the absorption coefficient as:

$$\kappa = (1 - \rho) \beta = \alpha \beta.$$  

(2.29)

The probability distribution of the scattered cosines $\mu_s$ allows the determination of the scattering phase function:

$$F_s(\mu_s) = \frac{1}{N_{\text{refl}}} \sum_{j=1}^{N_{\text{refl}}} \delta(\mu_s - \mu_{s,j}),$$

(2.30)

with $N_{\text{refl}}$ equals the number of rays which are extincted within $s_{\text{max}}$ and are reflected. The distribution can be computed for purely diffuse or perfectly specular reflection. The phase function is defined as the ratio of scattered intensity in a direction $s_s$ to the intensity in that direction for isotropic scattering and can be described by the following equation:

$$\Phi = \frac{\sum_{j=1}^{N_{\text{refl}}} \delta(\mu_s - \mu_{s,j})}{N_{\text{refl}}/n_{\text{bins}}} = n_{\text{bins}} \cdot F_s$$

(2.31)

with $n_{\text{bins}}$ the number of discrete directions. For the specular case, the scattering phase function is dependent on the reflectivity of the surface, which in turn is determined by the Fresnel’s Equations, and thus depends on the refractive index of solid ceria, which is a function of the wavelength.
Chapter 3

Snow

This chapter is dedicated to the study of snow microstructure. Two studies of different snow samples are provided. The first set of samples is composed of 5 different snow types representing a wide range of different microstructures. This study provides a first insight into the use of DPLS for the characterization of snow. The second set of samples consists of 34 snow samples which were already characterized experimentally in a previous study. The direct comparison to experimental values allows to assess the accuracy of DPLS for the determination of snow properties.

3.1 First characterization of snow samples

3.1.1 Introduction

As mentioned in Chapter 1, snow, a sintered porous material made of ice grains, has a complex porous microstructure that continuously changes with time and external conditions. Its effective mass transport properties, strongly dependent on the complex microstructure, are relevant for investigating a wide range of environmental processes. Its permeability has been investigated in various studies [8, 13, 35, 170, 177]. It is a measure of the pressure drop through a porous sample as a function of the velocity, for low velocities (Re<1). The Dupuit–Forchheimer coefficient is taken into account at a higher Reynolds number, when inertial effects become important [88].

Theoretical and empirical correlations for the determination of permeability have been developed for simplified two-phase media such as capillary, drag and the Carman–Kozeny models [45, 49, 88, 105], for fibrous beds [31, 42] and cellular foams [120]. No previous studies on the Dupuit–Forchheimer coefficient of snow were found; correlations were proposed for other porous materi-

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In previous studies \[52, 67, 69, 136\], micro-computed tomography (\(\mu\)CT) was applied to obtain the precise digital 3D geometrical representation of complex porous media, such as reticulate ceramic foams, porous rocks and packed beds of opaque or semi-transparent particles, and subsequently used in DPLS to calculate the effective transport properties. Recently, DPLS has been applied for the characterization of polar firn \[39\] and shown to describe with good accuracy morphological properties as supported by experimental validation. A fundamental advantage of DPLS compared with direct measurements is that stratigraphically complex snow samples with thin layers can also be characterized, leading to different properties for each layer, whereas an experimental measurement would yield only an average over the whole sample. In the present study, \(\mu\)CT is applied to obtain the 3D digital geometry of seasonal snow types. The governing mass and momentum conservation equations are numerically solved at the pore scale (DPLS) by the finite-volume method, allowing for the determination of the permeability and Dupuit–Forchheimer coefficient.

### 3.1.2 Morphological characterization

Five different snow samples are considered: decomposing snow (ds), metamorphosed snow I (mI), metamorphosed snow II (mII), depth hoar (dh), and wet snow (ws). They correspond to the grain shape classifications: DFdc, RGsr/DFdc, RGsr, DHcp and MFcl \[50\] and have been used in previous studies for the determination of their specific surface area \[90\] as well as their optical properties \[68\]. ds, mI and mII were prepared by sieving fresh snow after precipitation into boxes, which were then stored at different temperatures \[90\]. dh and ws were collected in the field; dh was collected in boxes, while ws was sieved and soaked with ice water \[90\]. The preparation of each sample is detailed in Table 3.1.

Tomographic scans were carried out with a Scanco \(\mu\)CT 80 desktop X-ray tomographic setup situated in a cold room at \(-15^\circ\text{C}\), with a microfocus X-ray source emitting a white spectrum at an acceleration voltage of 45 keV \[90\]. Each sample was scanned at 1000 angles over 180\(^\circ\). For each angle, two scans with an integration time of 0.25 s were averaged to reduce the noise. The data was then filtered with a \(3 \times 3 \times 3\) median filter and a \(3 \times 3 \times 3\) 3D Gaussian filter, and the gray values were segmented to separate them into void and solid phase. The voxel sizes were 10 mm for the ds, mI and mII snow samples, and 18 mm for the dh and ws samples, with a scanned volume of \(600 \times 600 \times 400\) voxels, corresponding to \(144\text{mm}^3\) and \(840\text{mm}^3\), respectively. Figure 3.1 depicts a 2D cross section and the 3D surface rendering of the 5 different snow samples.

Table 3.2 summarizes the morphological characteristics by experimen-
Figure 3.1: 2D cross section (left) and 3D rendering (right) of the 5 characteristic snow samples in the following order: ds, mI, mII, dh, ws. The edge length of the 2D cross sections is 6 mm for ds, mI and mII, and 10.8 mm for dh and ws.
Table 3.1: Description of the snow samples types. Name, type, grain shape classification [50], preparation [90].

<table>
<thead>
<tr>
<th>Sample</th>
<th>Type</th>
<th>ICSSG</th>
<th>Preparation</th>
</tr>
</thead>
<tbody>
<tr>
<td>ds</td>
<td>DFdc/2a</td>
<td>Decomposing</td>
<td>sieved, 8 days at -50°C</td>
</tr>
<tr>
<td>mI</td>
<td>RGsr(DFdc)/3a(2a)</td>
<td>Metamorphosed I</td>
<td>sieved, 14 days at -17°C</td>
</tr>
<tr>
<td>mII</td>
<td>RGsr/3a</td>
<td>Metamorphosed II</td>
<td>sieved, 17 days at -3°C</td>
</tr>
<tr>
<td>dh</td>
<td>DHcp/5a_2</td>
<td>Depth hoar</td>
<td>from field, not sieved</td>
</tr>
<tr>
<td>ws</td>
<td>MFcl/6a</td>
<td>Wet snow</td>
<td>from field, sieved, soaked with ice water</td>
</tr>
</tbody>
</table>

Table 3.2: Morphological characterization of snow samples. Measured snow density ($\rho_{ex}$) and voxel size [90], numerically determined porosity ($\varepsilon_n$), specific surface area ($A_{0,n}$), grain size ($d_{g,n}$), pore size ($d_{p,n}$) [68] and edge length of cubic REV ($l_{REV}$) for five characteristic snow samples: decomposing snow (ds), metamorphosed I (mI), metamorphosed II (mII), depth hoar (dh), and wet snow (ws).

<table>
<thead>
<tr>
<th>Sample</th>
<th>$\rho_{ex}$ g cm$^{-3}$</th>
<th>Voxel size $\mu$m</th>
<th>$\varepsilon_n$</th>
<th>$A_{0,n}$ m$^{-1}$</th>
<th>$d_{g,n}$ mm</th>
<th>$d_{p,n}$ mm</th>
<th>$l_{REV}$ mm</th>
</tr>
</thead>
<tbody>
<tr>
<td>ds</td>
<td>0.11 ± 0.01</td>
<td>10</td>
<td>0.854</td>
<td>8178</td>
<td>0.05</td>
<td>0.24</td>
<td>0.69</td>
</tr>
<tr>
<td>mI</td>
<td>0.15 ± 0.01</td>
<td>10</td>
<td>0.845</td>
<td>6450</td>
<td>0.08</td>
<td>0.27</td>
<td>0.83</td>
</tr>
<tr>
<td>mII</td>
<td>0.19 ± 0.03</td>
<td>10</td>
<td>0.805</td>
<td>5488</td>
<td>0.13</td>
<td>0.32</td>
<td>1.11</td>
</tr>
<tr>
<td>dh</td>
<td>0.31 ± 0.02</td>
<td>18</td>
<td>0.670</td>
<td>2777</td>
<td>0.40</td>
<td>0.75</td>
<td>1.81</td>
</tr>
<tr>
<td>ws</td>
<td>0.56 ± 0.03</td>
<td>18</td>
<td>0.384</td>
<td>3016</td>
<td>0.66</td>
<td>0.41</td>
<td>2.68</td>
</tr>
</tbody>
</table>

3.1.3 Methodology

DPLS of fluid flow across the five characteristic snow samples was performed. An in-house tetrahedron-based mesh generator was used to create the com-
putational grid directly on the µCT scans. A commercial CFD code [7] based on the finite volume technique was used to solve the continuity and Navier–Stokes equations. The computational domain, shown in Figure 3.2, consists of a square duct containing a sample of the porous material. The boundary conditions are: uniform inlet velocity and temperature and outlet pressure, no-slip and constant wall temperature at the solid-fluid interface, and symmetry at the lateral duct walls. The 2nd order Darcy’s law (Equation 2.16) is used to determine permeability and Dupuit–Forchheimer coefficient. The characteristic length scale, $d$, used throughout this study is the numerically calculated pore diameter (see Table 3.2). A linear least-square-fitting method was used to fit the numerically calculated Re-dependent $\Pi_{pg}$ in Equation 2.19, allowing for the determination of $K$ and $F$.

![Figure 3.2: Computational domain of the DPLS.](image)

### 3.1.4 Convergence and Accuracy

Figure 3.3 shows an example of the convergence value of the length of cubic REV calculated based on porosity for the wet snow sample with $\xi = 0.05$. The lengths of cubic REV based on porosity for the five snow samples are listed in Table 3.2 and are 2.4 to 13.8 times larger than the calculated pore and particle diameter, respectively. dh needs a relatively small REV while ws needs a relatively large REV compared with their characteristic lengths. REV calculated based on pressure drop – and consequently on permeability and Dupuit–Forchheimer – coefficient is also shown in Figure 3.3, which indicates that larger REVs are required. The need for larger REV based on heat transfer properties was previously discussed [67].

Therefore, preliminary calculations were carried out for various sample sizes and mesh element sizes of the subset to elucidate the trade-off between
computational time and accuracy of the results. First, different sample sizes are considered, with the size in $x$ and $y$ fixed at 600 voxels (10.8 mm for dh and ws, 6 mm for ds, mI and mII), while $z$ size is varied from 50 to 400 voxels (0.9 to 7.2 mm for dh and ws, 0.5 to 4 mm for ds, mI and mII). Pressure drop and mean velocity are calculated for each sample size. It has been observed that the slope of the pressure drop and of the velocity converge rapidly after a small entrance length [114]; this allows to keep the length parallel to the flow shorter than the two other lengths of the sample. Previous calculations varying the $x$ and $y$ sizes showed that the results were more precise when using the maximum possible length in those directions (i.e. 600 voxels). Therefore, only the $z$ size is varied for the REV determination, while $x$ and $y$ are kept to a size of 600 voxels. For each sample size, pressure drop and mean velocity are compared to the largest vertical sample size of 400 voxels. Figures 3.4 and 3.5 show the values of pressure drop and mean velocity, respectively, corresponding to different increasing values of $z$ size. Velocity converged more rapidly than pressure drop.

The same procedure is applied to choose the mesh element length. With a fixed sample size, the number of mesh refinements is varied from 500 µm to 62.5 µm for ds, mI and mII and from 900 µm to 112.5 µm for dh and ws. Figures 3.6 and 3.7 show the values of pressure drop and mean velocity, respectively, corresponding to different decreasing values of the largest mesh element length. As for the sample size, the velocity converged more rapidly than pressure drop.
3.1. FIRST CHARACTERIZATION OF SNOW SAMPLES

Figure 3.4: Pressure drop vs vertical length of the sample (z size), for each of the 5 representative snow samples. The horizontal length (x and y sizes) are kept fixed to 600 voxels, corresponding to 6 mm for ds, mI and mII, and to 10.8 mm for dh and ws. The largest mesh element length is kept fixed to a size of 125 μm for ds, mI and mII and 225 μm for dh and ws.

Figure 3.5: Velocity vs vertical length of the sample (z direction), for each of the 5 representative snow samples. The horizontal length (x and y directions) are kept fixed to 600 voxels, corresponding to 6 mm for ds, mI and mII, and to 10.8 mm for dh and ws. The largest mesh element length is kept fixed to a size of 125 μm for ds, mI and mII and 225 μm for dh and ws.
Figure 3.6: Pressure drop vs mesh element length, for each of the 5 representative snow samples. The sample is kept to a size of $600 \times 600 \times 200$ voxels ($6 \times 6 \times 2$ mm for ds, mI and mII, $10.8 \times 10.8 \times 3.6$ for dh and ws), while the largest mesh element size is varied from 500 $\mu$m to 62.5 $\mu$m for ds, mI and mII and from 900 $\mu$m to 112.5 $\mu$m for dh and ws.

Figure 3.7: Velocity vs mesh element length, for each of the 5 representative snow samples. The sample is kept to a size of $600 \times 600 \times 200$ voxels ($6 \times 6 \times 2$ mm for ds, mI and mII, $10.8 \times 10.8 \times 3.6$ for dh and ws), while the largest mesh element size is varied from 500 $\mu$m to 62.5 $\mu$m for ds, mI and mII and from 900 $\mu$m to 112.5 $\mu$m for dh and ws.
3.1. **FIRST CHARACTERIZATION OF SNOW SAMPLES**

A representative sample size of $600 \times 600 \times 200$ voxels ($10.8 \times 10.8 \times 3.6$ mm$^3$) with a largest mesh element size of 225 mm was chosen for ws and dh samples. For ds and mI samples, the chosen sample size was $600 \times 600 \times 300$ voxels ($6 \times 6 \times 3$ mm$^3$) with a largest mesh element size of 125 mm. For the mII sample, the sample size was $600 \times 600 \times 200$ voxels ($6 \times 6 \times 2$ mm$^3$) with a largest mesh element size of 125 mm. Convergence was achieved for a termination residual root mean square (RMS) of the iterative solution below $9 \times 10^5$. The sample sizes were chosen with a relative difference of pressure drop with the highest possible size between 1.7% and 6.2%, whereas the largest mesh element sizes were chosen with a relative difference of pressure drop with the smallest possible mesh element between 2.8% and 10.3%.

### 3.1.5 Results and Discussion

The dimensionless pressure gradient $\Pi_{pg}$ is plotted as a function of Re in Figure 3.8 for the five snow samples.

![Figure 3.8: Calculated (symbols) and fitted (curves) dimensionless pressure gradient as a function of Re for the five characteristic snow samples.](image)

The calculated permeability $K$ and Dupuit–Forchheimer coefficient $F$ are plotted in Figure 3.9 versus the pore diameter; their values and the goodness of fit are listed in Table 3.3.

$K$ is lowest and $F$ highest for the ws sample, as its density is highest and porosity lowest. On the other hand, $K$ increases with ds, mI, mII and dh samples because of the increasing pore size, which reduces pressure loss and
Table 3.3: Values of $K$ and $F$ obtained by DPLS, calculated using the pore size.

<table>
<thead>
<tr>
<th></th>
<th>ds</th>
<th>mI</th>
<th>mII</th>
<th>dh</th>
<th>ws</th>
</tr>
</thead>
<tbody>
<tr>
<td>$K$ [m$^2$]</td>
<td>$2.73 \cdot 10^{-9}$</td>
<td>$2.73 \cdot 10^{-9}$</td>
<td>$3.27 \cdot 10^{-9}$</td>
<td>$1.01 \cdot 10^{-8}$</td>
<td>$8.49 \cdot 10^{-10}$</td>
</tr>
<tr>
<td>$F$ [m$^{-1}$]</td>
<td>$1.94 \cdot 10^3$</td>
<td>$1.60 \cdot 10^3$</td>
<td>$1.49 \cdot 10^3$</td>
<td>$2.40 \cdot 10^3$</td>
<td>$3.48 \cdot 10^4$</td>
</tr>
<tr>
<td>RMS</td>
<td>2.53</td>
<td>2.80</td>
<td>4.61</td>
<td>9.11</td>
<td>18.45</td>
</tr>
</tbody>
</table>

Figure 3.9: Permeability and Dupuit–Forchheimer coefficient versus pore diameter.
leads to a higher $K$ and a smaller $F$ [67]. The unexpected decrease of ws in $K$ and increase in $F$ highlights that one morphological characteristic (e.g. $d_{pore}$) does not describe sufficiently well the microstructure and supports the importance of the CT-based determination of the effective mass transport properties.

The values of $K$ and $F$ of Table 3.3 are compared with theoretical and empirical models using simplified microstructure:

Conduit flow model for a Hagen-Poiseuille flow [45,88]:

$$K = \frac{\varepsilon d_{pore}^2}{32}$$

(3.1)

Hydraulic radius model based on the Carman–Kozeny equation [45,88]:

$$K = \frac{\varepsilon^3}{5(1 - \varepsilon)^2A_0^2}$$

(3.2)

Empirical models for fibrous beds by Davies [45]:

$$K = \frac{d_{grain}^2}{64(1 - \varepsilon)^{3/2}(1 + 56(1 - \varepsilon)^3)}$$

(3.3)

Empirical models for fibrous beds by Chen [31,45]:

$$K = \frac{\pi d_{grain}^2 \ln(k_5/(1 - \varepsilon)^2)}{4k_4}\frac{\varepsilon}{1 - \varepsilon}$$

with $k_4 = 6.1, k_5 = 0.64$

(3.4)

Shimizu function [170]:

$$K_{Shimizu} = 0.077 d_{grain}^2 e^{-0.0078 \rho}$$

(3.5)

Extension of hydraulic radius theory of Carman–Kozeny [49,105]:

$$F = 1.8 \frac{1 - \varepsilon}{\varepsilon^3 \frac{1}{d_{pore}}}$$

(3.6)

Empirical correlation for cellular foams [120]:

$$F = \frac{1.8 \cdot 10^4 (1 - \varepsilon)}{\varepsilon^3 d_0^{0.24}_{pore}}$$

(3.7)

Model relating the Dupuit–Forchheimer coefficient to the permeability [88]:

$$F = \frac{0.55}{\sqrt{K}}$$

(3.8)
The $K$ and $F$ of the five characteristic snow samples, calculated by the CT-based DPLS method (Table 3.3) and by the simplified models of Equations (3.1)-(3.8), are shown in Figures 3.10 and 3.11, respectively.

![Figure 3.10: Permeability (dimensionless, $K/d_{\text{grain}}^2$) as a function of snow density for CT-based DPLS and for theoretical and empirical models.](image)

![Figure 3.11: Dupuit–Forchheimer coefficient as a function of snow density for CT-based DPLS and for theoretical and empirical models.](image)

The conduit flow model, Equation (3.1), compares well with DPLS for $m_I$, $m_{II}$, $dh$ and $ds$, particularly for $dh$ (relative difference to DPLS of 17%). DPLS gives results close to those of the fibrous bed model for all types of snow (relative difference to DPLS from 18% for $ws$ to 77% for $ds$). Shimizu [170], Equation (3.5), gives values comparable to DPLS for all types of snow, but with a higher relative difference for most of them (from 41% for $ds$ to 97% for $ws$). Equations (3.2) and (3.4) give results far from DPLS, with relative differences up to 4300% and 6000%, respectively. It has been shown that the Carman–Kozeny model does not fit to experimental data when the porous medium has high porosity, its particles are far from a spherical shape, or the porous medium is consolidated [111], which is the case for snow.

Equation (3.6) compares well with $F$ values found with DPLS, in particular for $m_I$, $dh$ and $ds$, for which relative differences to DPLS are only 7%, 10% and 9%, respectively. The values obtained from Equation (3.7) compare well with that of DPLS, in particular for $ws$ (relative difference of 14%). Finally, Equation (3.8) gives results comparable to DPLS for $ws$ (relative difference to DPLS of 46%), but not for the other types of snow.

The permeability obtained by DPLS can also be compared to Lattice-Boltzmann modeling of permeability in firn [39]. However, these results have to be taken cautiously, as the samples analyzed do not come from the same
3.1. FIRST CHARACTERIZATION OF SNOW SAMPLES

snow. Firn has generally higher grain sizes than those studied here; however, ws can be similar to small-grained firn. Permeability of ws is compared with Lattice–Boltzmann results in Table 3.4. Results are similar, however, for similar grain diameter, specific surface area is much higher in firn than in ws. This could explain the higher firn permeability. Again, this difference in specific surface area shows the high differences in microstructure.

Table 3.4: Comparison of ws permeability calculated from DPLS with firn permeability obtained by Lattice–Boltzmann modeling [39]

<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
<th>Difference of K with ws</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>m⁻¹</td>
<td>mm</td>
<td>m²</td>
<td>%</td>
</tr>
<tr>
<td>ws</td>
<td>3016</td>
<td>0.384</td>
<td>0.66</td>
<td>8.49·10⁻¹⁰</td>
</tr>
<tr>
<td></td>
<td>7143</td>
<td>0.43</td>
<td>1.20</td>
<td>1.19·10⁻⁹</td>
</tr>
<tr>
<td></td>
<td>5882</td>
<td>0.43</td>
<td>1.31</td>
<td>1.67·10⁻⁹</td>
</tr>
<tr>
<td></td>
<td>7143</td>
<td>0.58</td>
<td>0.59</td>
<td>1.13·10⁻⁹</td>
</tr>
<tr>
<td></td>
<td>5882</td>
<td>0.57</td>
<td>0.83</td>
<td>2.60·10⁻⁹</td>
</tr>
<tr>
<td></td>
<td>6667</td>
<td>0.53</td>
<td>0.79</td>
<td>1.66·10⁻⁹</td>
</tr>
</tbody>
</table>

Experimental data on the permeability of snow are scarce because handling and precise measurements are difficult. This is especially true for the more permeable snow types, e.g. depth hoar. For these snow types, DPLS will possibly become the method of choice because µCT of samples casted with diethyl-phthalate has become possible [72]. Snow is often anisotropic at different scales. Even a homogeneous sample may be anisotropic in permeability at the pore level, which is accounted for in Equation (2.14) when introducing a permeability tensor $K$. The technique applied in this study is able to capture effects as previously shown for porous ceramic structures [67]. At a larger scale, snow is highly layered at the mm-scale [138], therefore pore-level anisotropy is usually masked when measuring anisotropy in the field. DPLS is able to detect these effects and would therefore be advantageous to experimental techniques.

3.1.6 Anisotropy

An additional study has been performed to calculate the anisotropy of permeability and Dupuit–Forchheimer coefficient. In this study, the same methodology as before is applied, by changing the air flow direction from vertical to

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Material from this section has been extracted from the semester project of Yi Cheng Ng, entitled *Pore-level Determination of Permeability and Dupuit-Forchheimer Coefficient’s Anisotropy in Characteristic Snow Samples*, 2011. This project was directly supervised by E. Zermatten.
horizontal. A convergence study is again performed in the horizontal direction. The resulting chosen samples size and mesh element size are shown in Table 3.5.

Table 3.5: Representative sample sizes and largest mesh element length, for each of the 5 representative snow samples.

<table>
<thead>
<tr>
<th>Snow type</th>
<th>Sample size [mm$^3$]</th>
<th>Mesh element size [µm]</th>
</tr>
</thead>
<tbody>
<tr>
<td>ds</td>
<td>$3.5 \times 6.0 \times 4.0$</td>
<td>125</td>
</tr>
<tr>
<td>mI</td>
<td>$4.0 \times 6.0 \times 4.0$</td>
<td>125</td>
</tr>
<tr>
<td>mII</td>
<td>$3.0 \times 6.0 \times 4.0$</td>
<td>125</td>
</tr>
<tr>
<td>dh</td>
<td>$6.3 \times 10.8 \times 7.2$</td>
<td>180</td>
</tr>
<tr>
<td>ws</td>
<td>$7.2 \times 10.8 \times 7.2$</td>
<td>225</td>
</tr>
</tbody>
</table>

$K$ and $F$ in both directions are shown in Table 3.6 along with their anisotropy coefficient, defined by $A(K) = K_z/K_x$. $A(K)$ range from 1.03 to 1.18, which is consistent with literature, as Calonne et al. [30] obtained values from 0.74 to 1.66, whereas Luciano et al., [103] had results between 0.75 and 1.9. The horizontal permeability, $K_x$, is systematically lower than the vertical one ($K_z$). This could result from the vertical deformation of snow due to gravity, increasing the vertical permeability [103].

The values of $A(F)$ were lower than 1 for ds, mI and mII, and higher than 1 for dh and ws. By looking at the preparation of the samples, one can see that ds was stored at a very low temperature (-50°C) for only 8 days, and therefore did not undergo strong metamorphism. As a result, $A(F)$ for ds is close to 1. mI and mII went through more metamorphism, being both stored at higher temperatures and for longer times (14 days at $-17°C$ for mI, 17 days at $-50°C$). Therefore, their anisotropy coefficient for $F$ is smaller than the one of ds. The preparation procedure for dh and ws was completely different, therefore resulting in a different anisotropy. Both were not stored, but directly used in the measurements. dh was collected from the field without sieving, whereas ws was sieved and soaked with ice water. These preparation resulted in a higher vertical permeability, and a strong anisotropy in $F$, particularly for ws, which water content seems to have increased the anisotropy in $F$. This is however not the case for the anisotropy in $K$, dh and ws having the smallest one amongst all of the samples.

3.1.7 Summary and Conclusions

Mass transfer properties, namely permeability ($K$) and Dupuit–Forchheimer coefficient ($F$), were determined for five characteristic snow samples. The methodology consisted of first obtaining the complex 3D geometrical representation of the snow microstructure by computer tomography. The µCT
Table 3.6: Values of $K$ and $F$ in horizontal and vertical directions, along with their anisotropy coefficient ($A(K) = K_z/K_x$), for each of the 5 representative snow samples.

<table>
<thead>
<tr>
<th>Snow type</th>
<th>$K_x$ [m$^2$]</th>
<th>$K_z$ [m$^2$]</th>
<th>$A(K)$</th>
<th>$F_x$ [m$^{-1}$]</th>
<th>$F_z$ [m$^{-1}$]</th>
<th>$A(F)$</th>
</tr>
</thead>
<tbody>
<tr>
<td>ds</td>
<td>$2.58 \cdot 10^{-9}$</td>
<td>$2.73 \cdot 10^{-9}$</td>
<td>1.06</td>
<td>$2.07 \cdot 10^3$</td>
<td>$1.94 \cdot 10^3$</td>
<td>0.94</td>
</tr>
<tr>
<td>mI</td>
<td>$2.31 \cdot 10^{-9}$</td>
<td>$2.73 \cdot 10^{-9}$</td>
<td>1.18</td>
<td>$1.98 \cdot 10^3$</td>
<td>$1.60 \cdot 10^3$</td>
<td>0.81</td>
</tr>
<tr>
<td>mII</td>
<td>$2.90 \cdot 10^{-9}$</td>
<td>$3.27 \cdot 10^{-9}$</td>
<td>1.13</td>
<td>$1.78 \cdot 10^3$</td>
<td>$1.49 \cdot 10^3$</td>
<td>0.84</td>
</tr>
<tr>
<td>dh</td>
<td>$9.76 \cdot 10^{-9}$</td>
<td>$1.01 \cdot 10^{-8}$</td>
<td>1.03</td>
<td>$1.95 \cdot 10^3$</td>
<td>$2.40 \cdot 10^3$</td>
<td>1.23</td>
</tr>
<tr>
<td>ws</td>
<td>$8.28 \cdot 10^{-10}$</td>
<td>$8.49 \cdot 10^{-10}$</td>
<td>1.03</td>
<td>$2.37 \cdot 10^4$</td>
<td>$3.48 \cdot 10^4$</td>
<td>1.47</td>
</tr>
</tbody>
</table>

scans were digitalized and used in direct pore-level simulations (DPLS). An in-house tetrahedron-based mesh generator was used to create the computational grid directly on the µCT data. Mass and momentum conservation equations were numerically solved at the pore scale by the finite-volume method. Pressure drop over the snow sample was determined and fitted to the Darcy’s law extended by the Dupuit–Forchheimer term (Equation (2.16)), allowing for the determination of $K$ and $F$. A larger pore size led to higher $K$, except for wet snow, for which a large pore size was compensated by a low porosity and high density.

As expected, the low $K$ of wet snow led to a high $F$. The values of $K$ and $F$ computed by DPLS were compared with those obtained by analytical and empirical models of porous media with simplified microstructure. The Conduit flow model compared particularly well with DPLS for four types of snow. Shimizu’s prediction gave reasonable comparisons. The extension of the hydraulic radius theory for $F$ yielded particularly good results compared with DPLS for three types of snow. $K$ and $F$ were also calculated with a horizontal air flow, to determine their anisotropy. $K$ horizontal was systematically lower than $K$ vertical, while $F$ did not show the same trend. The anisotropy coefficients of $K$ showed values consistent with literature. The anisotropy coefficients of $F$ varied depending on the snow preparation. The applied methodology is able to accurately account for the complex snow microstructure, which cannot be described by only a few morphological characteristics such as porosity, pore or particle size. Furthermore, it can be applied to investigate anisotropy on multiple scales. The calculated effective transport properties can be readily applied in volume-averaged (continuum) models of snowpack for a wide range of environmental applications.
3.2 Second characterization of snow samples

3.2.1 Introduction

Recently, permeability, porosity, and specific surface per unit mass were measured for a large number of different samples [8]. A matching correlation was found between their microstructural parameters, but substantial uncertainty remains. As the samples of this latter study were cast with dimethyl phthalate (DMP) and conserved, it was possible to scan them later by sublimation tomography [72] in order to conduct the present study.

The method of casting snow with diethyl or dimethyl phthalate allows the microstructure to be kept stable and later analysis by µCT, where the use of a permeameter would not be possible anymore after the snow is cast. DPLS allows the determination of pore size, which provides a better parameterization of permeability than grain size [39,152].

Previous studies on snow permeability applied the linear Darcy’s law [40]. However, it has been shown that this law only approximates the pressure drop during laminar flow in porous media [95,156,175,179], even at low fluid velocities. In the present study, the 3rd order extended form of Darcy’s law (Equation 2.17) is applied [156].

The objective of the present section is to show the validity of the methodology presented in Section 3.1 and assess its accuracy by comparing DPLS results to the experimental values of permeability obtained from 34 snow sample [8]. Calculations were also performed to determine the threshold air flow velocity for which the second and third order corrections become important in the extended Darcy’s law. Recently, increased attention was directed to the anisotropic permeability of snow [30,78,149], which is difficult to examine via physical measurements. In this paper, anisotropy of permeability is also examined via DPLS.

Computational fluid dynamics (CFD) has also been applied for the characterization of polar firn [39] with a comparison to measurements. A more recent study uses numerical computation to determine snow permeability and anisotropy in permeability of several snow samples [30], but only comparing parameterizations from experimental results. As there exists an infinity of different snow structures that cannot be described by simple morphological properties, our comparison with the same snow samples will give a direct validation of the DPLS methodology and better understanding of its limitations.

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3Material from this section has been published in: E. Zermatten, M. Schneebeli, H. Arakawa and A. Steinfeld, Tomography-based determination of porosity, specific area and permeability of snow and comparison with measurements. Cold Regions Science and Technology, 97, pp.33–40, 2014.
3.2.2 Snow replicas

To preserve the snow microstructure, samples can be cast with diethyl phthalate (DEP) or dimethyl phthalate (DMP) and frozen at $-60 \, ^\circ C$ to preserve their original structure and to allow their transportation and storage. In the present study, DMP was used to preserve the samples. Sublimation tomography [72] is then used to characterize the samples.

Between $-20 \, ^\circ C$ and $0 \, ^\circ C$, the vapour pressure of ice is about $100 \, \text{Pa}$ [216], whereas the vapour pressure of DMP is about $10^{-2} \, \text{Pa}$ [216]. These properties allow to sublimate the ice without modifying the structure of DMP. Note that DEP is giving even better results, with a vapour pressure of about $10^{-4} \, \text{Pa}$ at the same temperature range.

First, the complete sample is scanned using a Scanco-\textmu CT 40 CT. This way, the air bubbles that could have been trapped in DMP during the casting process are also imaged. Figure 3.12 (left) show a slice of a snow sample casted in DMP, before the sublimation process. The air bubbles trapped in DMP are clearly visible on the image. All the scanning procedure is done at $-20 \, ^\circ C$.

The ice is then sublimated from the sample by lowering the pressure to about $10^{-2} \, \text{mbar}$, always at $-20 \, ^\circ C$. Silica gel is placed above the sample to absorb the water and to accelerate the process. The remaining is only the frozen DMP structure, which fills the former void space, and is therefore a ‘negative’ of the sample. This DMP structure is then scanned again. Figure 3.12 (right) shows the same sample slice as Figure 3.12 (left) after the sublimation process. The image of the pore space and the image of the snow matrix are superimposed and the air bubbles trapped in the DMP are removed by image processing. The resulting image is inverted.

A threshold is set to separate the gray values into ice and void phase. Figure 3.13 shows a sample slice being segmented (left) along with the histogram of its gray values (right). The 3D rendering of a sample at the end of the sublimation tomography process is shown in Figure 3.14.

3.2.3 Method

More than a hundred different snow samples were collected during the winter 2007-2008 in Hokkaido prefecture, Japan [8]. Each of these samples was cast with DMP and stored at $-40 \, ^\circ C$. We scanned a subset of 34 samples using sublimation tomography [72], with a voxel edge length of 10 \textmu m. The scanned samples had a dimension around $8\times8\times8 \, \text{mm}^3$. A threshold was set to separate the gray values into ice and void phase. Two-point correlation function [67, 136] was used to determine morphological properties, namely: the porosity ($\varepsilon$) and specific surface area (SSA), here defined as the phase boundary surface divided by the total snow volume. We determined the REV based on modeled
Figure 3.12: Slice of a snow/DMP sample before (left) and after (right) the sublimation of ice.

Figure 3.13: Segmentation process; cross section of a sample being segmented (left) and histogram of the gray values (right)
3.2. SECOND CHARACTERIZATION OF SNOW SAMPLES

Figure 3.14: 3D visualization of a snow sample obtained by sublimation tomography

pressure drop and velocity calculations for subsequently growing volumes until the pressure drop and the velocity asymptotically reached a constant value within a given error band.

Each 3D image was meshed using an in-house mesh generator [55]. For each sample, the largest mesh element length was 0.25 mm and the smallest possible mesh element measured 15.625 µm. This refinement was chosen after a grid convergence study with a tolerance of 5% for the calculated pressure drop. Preliminary calculations of the REV were carried out for various sample sizes to elucidate the trade-off between computational time and accuracy of the results. It was observed in previous section (3.1) that the width of the sample parallel to the flow direction can be chosen 2 to 3 times shorter than the perpendicular lengths without jeopardizing the precision of the results [217]. For the determination of $K$ and $F$, it has been shown [67, 217] that it is not sufficient to base the calculation of the REV simply on porosity, as the calculations based on pressure drop give larger REVs than the ones based on porosity. One REV was chosen for each snow type (Table 3.7) after performing preliminary calculations on one sample of each type. All the simulations were performed along the vertical and the horizontal axis of the samples, which are both principal axes of the snow [102, 150]. The sample was always cut in order to have the shortest length parallel to the flow direction.

A CFD code based on the finite volume technique [7] was applied to solve the 3D Navier-Stokes equations. The computational domain consisted of a
square duct containing a sample of snow. The boundary conditions consisted of uniform inlet velocity and temperature, outlet pressure, no-slip velocity and constant wall temperature at the solid-fluid interface, and symmetry of the sample at the lateral duct walls. The square duct, which measured 5 times the length of the sample, was added to ensure a fully developed velocity profile at the entrance of the snow sample (Figure 3.15).

In this study, Equation (2.17) is used. The fits to Equation (2.15) and (2.16) were also tested, assuming a transitional Re=1. However, the goodness of the fit was better for Equation (2.17). For comparison, $K$ is also calculated according to the linear form of Darcy’s law (Equation (2.14)). $\Pi_{pg}$ from Equation 2.18 is calculated for different values of Re and least-square-fitted to determine $K$, $F$ and $\gamma$. The chosen characteristic length is the equivalent pore diameter, $d = 6\varepsilon/\text{SSA}$ [45]. It was preferred to a pore size based on opening size distribution, as it might not characterize well the size of non-spherical particles. The values were computed for an air density of 1.185 kg/m$^3$ and a dynamic viscosity of $1.831 \cdot 10^{-5}$ kg/(m·s). These simulations are first done in the vertical direction of the samples, and then in the horizontal direction for 14 of the samples. The results obtained for $K$ in vertical direction are compared to the measured data obtained by Arakawa by applying the linear form of Darcy’s law [8].

![Figure 3.15: Schematic of the computational domain with an enlarged sub-sample of snow. In the snow sample, the dark gray part represents the ice, whereas the mesh is built in the pore space.](image)

### 3.2.4 Results

All of the simulations were carried out using the REVs given in Table 3.7. As observed previously [217], the width of the sample parallel to the flow
can be chosen smaller than the two other directions without jeopardizing the accuracy of the results.

Table 3.7: Representative elementary volume for each snow type.

<table>
<thead>
<tr>
<th>Snow Type</th>
<th>REV [mm$^3$]</th>
</tr>
</thead>
<tbody>
<tr>
<td>△△</td>
<td>7 × 7 × 2</td>
</tr>
<tr>
<td>□□</td>
<td>6 × 6 × 2</td>
</tr>
<tr>
<td>●●</td>
<td>6 × 6 × 2</td>
</tr>
<tr>
<td>//</td>
<td>6 × 6 × 4</td>
</tr>
<tr>
<td>□□□</td>
<td>6 × 6 × 5</td>
</tr>
</tbody>
</table>

The SSA calculated in the present study by two-point correlation function is plotted in Figure 3.16 versus the SSA determined by Arakawa by the method of model-based stereology [8]. The SSA from the scanned samples and SSA from sections had relative differences with an average of 18% and a standard deviation of 18%.

Table 3.8: List of the snow samples with their properties compared in this study.

<table>
<thead>
<tr>
<th>Sample #</th>
<th>Snow Type</th>
<th>Density measured by Arakawa [8] [kg/m$^3$]</th>
<th>SSA measured by stereology [mm$^2$/m$^3$]</th>
<th>Permeability measured by Arakawa [8] [m$^2$]</th>
<th>SSA simulated by DPLS within this study [mm$^2$/m$^3$]</th>
<th>Permeability simulated by DPLS within this study [m$^2$]</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>△△</td>
<td>261</td>
<td>2619</td>
<td>9.51 × 10$^{-9}$</td>
<td>3227</td>
<td>1.13 × 10$^{-8}$</td>
</tr>
<tr>
<td>2</td>
<td>□□</td>
<td>259</td>
<td>3927</td>
<td>2.71 × 10$^{-9}$</td>
<td>5205</td>
<td>2.37 × 10$^{-9}$</td>
</tr>
<tr>
<td>3</td>
<td>△△</td>
<td>273</td>
<td>3310</td>
<td>4.97 × 10$^{-9}$</td>
<td>3905</td>
<td>6.47 × 10$^{-9}$</td>
</tr>
<tr>
<td>4</td>
<td>●●</td>
<td>385</td>
<td>5630</td>
<td>6.20 × 10$^{-10}$</td>
<td>7545</td>
<td>3.69 × 10$^{-10}$</td>
</tr>
<tr>
<td>5</td>
<td>●●</td>
<td>481</td>
<td>6194</td>
<td>2.70 × 10$^{-10}$</td>
<td>6960</td>
<td>2.91 × 10$^{-10}$</td>
</tr>
<tr>
<td>6</td>
<td>●●</td>
<td>366</td>
<td>7127</td>
<td>2.60 × 10$^{-10}$</td>
<td>8845</td>
<td>3.32 × 10$^{-10}$</td>
</tr>
<tr>
<td>7</td>
<td>//</td>
<td>296</td>
<td>5847</td>
<td>6.10 × 10$^{-10}$</td>
<td>8551</td>
<td>7.32 × 10$^{-10}$</td>
</tr>
<tr>
<td>8</td>
<td>//</td>
<td>217</td>
<td>5569</td>
<td>1.13 × 10$^{-9}$</td>
<td>6627</td>
<td>1.81 × 10$^{-9}$</td>
</tr>
</tbody>
</table>
Arakawa [8] measured the density of the snow samples by gravimetry. By converting his density values to porosity \( \varepsilon = 1 - \rho_{\text{snow}}/\rho_{\text{ice}} \), we can compare them to the values of porosity determined in the present study by two-point correlation function. The comparison of the two porosities is shown in Figure 3.17. The simulated values differed by an average of \(-3.14\%\) and a standard deviation of \(7.7\%\) from the measured values.

\( K \) values computed using DPLS and by applying the extended Darcy’s law (denoted as ‘simulated’) are presented in Figure 3.18 versus the measured values for each of the 34 samples. The measured values were obtained in a previous study [8] using an air permeameter to measure pressure, which was then used to deduce \( K \) by applying the linear Darcy’s law (2.14) assuming a Darcian velocity. The permeameter was custom-made with a double-head design. The computed and measured permeabilities had relative differences
3.2. SECOND CHARACTERIZATION OF SNOW SAMPLES

Figure 3.16: SSA obtained by two-point correlation function in the present study, vs SSA obtained by 2D stereology by Arakawa [8].

Figure 3.17: Porosity obtained by two-point correlation function in the present study, vs porosity calculated from the density measured by Arakawa [8].

with an average of 2.8% and a standard deviation of 46.7%. The values of $K$ obtained by DPLS range from $2.05 \cdot 10^{-10}$ m$^2$ to $1.95 \cdot 10^{-8}$ m$^2$.

$K$ obtained by DPLS and $K$ measured are plotted in Figure 3.19 as a function of the SSA obtained by DPLS. $K$ decreases with SSA for both simulated and measured values.

The following fit was obtained for $K$:

$$K = 2.55r_e^2e^{-0.012\rho}$$

(3.9)

where $r_e = 3(1 - \varepsilon)/$SSA is the equivalent sphere radius of a grain and $\rho = (1 - \varepsilon)\rho_{ice}$ is the density of the snow. The normalized root mean square error (NRMSE) of the fit was 0.13.

The dimensionless pressure gradient is plotted as a function of Re in Figure 3.20, along with the fit to (2.18) with an average NRMSE of 0.046. As a comparison, the fits using (2.15) for Re < 1 and (2.16) for Re > 1 had an average NRMSE of 0.27 and 0.14, respectively.

The literature indicates a deviation from linearity of the extended Darcy’s law (2.17) even at Re < 1 [95, 175]. To examine this effect, permeabilities were also calculated using DPLS and by applying the linear form of Darcy’s law (2.14) for entering velocities of 0.001 m/s, 0.05 m/s and 0.1 m/s, with corresponding Re in the range $0.02 - 0.11$, $1 - 5.56$, and $2 - 11.12$, respectively, and mean Re of 0.05, 2.68, and 5.37, respectively (Table 3.10). The values of $K$ are doubled between 0.05 m/s and 0.1 m/s. $K$ values with an entering velocity of 0.05 m/s are consistently lower than the ones measured at 0.001
CHAPTER 3. SNOW

Figure 3.18: Simulated permeabilities, obtained in the present study by DPLS, vs permeabilities measured by Arakawa [8].

Figure 3.19: Permeability simulated in this study by DPLS and permeability measured by Arakawa [8] as a function of the two-point correlation SSA simulated by DPLS.
m/s. They show a difference up to 16%. The measured $K$ [8], which had been derived by applying (2.14), are closer to the results measured with 0.05 m/s.

$F$ and $\gamma$ obtained by DPLS along the vertical axis are plotted as a function of porosity in Figure 3.21. $F$ decreases with an increasing porosity, but remains almost constant between a porosity of 0.7 and 0.9. $\gamma$ shows two different tendencies: some of the samples show the same behavior as $F$, whereas the other ones show a slight increase with porosity. $F$ increases with SSA.

To our knowledge, no correlation is available in the literature for the second and third order corrections to Darcy’s law in snow. $F$ and $\gamma$ were best fit using the density of the snow:

$$F = 5.98 \cdot 10^{-7} \rho^2 e^{-1500r_e}$$  \hspace{1cm} (3.10)

$$\gamma = 5.95 \cdot 10^{-3} \rho^2 e^{-2708r_e}$$  \hspace{1cm} (3.11)

Tortuosity as a function of Re is plotted in Figure 3.22 for 5 samples, one of each snow type. Tortuosity, which is also a factor influencing permeability, decreases with an increasing entering Re.

$K$ in vertical and horizontal direction is plotted as a function of porosity in Figure 3.23. The anisotropy coefficients, $A(K) = K_z/K_x$, had an average of 0.79 with a standard deviation of 0.41. A similar study was made for $F$ as
Table 3.10: Relative differences between the simulated permeability $K_{DPLS}$, calculated using DPLS and by applying the linear Darcy’s law (Equation 2.14) with entering velocities of 0.001 m/s, 0.05 m/s and 0.1 m/s, and the measured permeability $K_{measured}$ measured by Arakawa [8].

<table>
<thead>
<tr>
<th>Simulated results</th>
<th>min (%)</th>
<th>max (%)</th>
<th>average (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Relative differences between $K_{DPLS}(v=0.001\text{ m/s})$ and $K_{DPLS}(v=0.05\text{ m/s})$</td>
<td>1.6</td>
<td>16.2</td>
<td>3.6</td>
</tr>
<tr>
<td>Relative differences between $K_{DPLS}(v=0.05\text{ m/s})$ and $K_{DPLS}(v=0.1\text{ m/s})$</td>
<td>50</td>
<td>50</td>
<td>50</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Simulated vs measured results</th>
<th>min (%)</th>
<th>max (%)</th>
<th>average (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Relative differences between $K_{DPLS}(v=0.001\text{ m/s})$ and $K_{measured}$</td>
<td>1.4</td>
<td>546.8</td>
<td>55.6</td>
</tr>
<tr>
<td>Relative differences between $K_{DPLS}(v=0.05\text{ m/s})$ and $K_{measured}$</td>
<td>1.4</td>
<td>517.2</td>
<td>47.4</td>
</tr>
<tr>
<td>Relative differences between $K_{DPLS}(v=0.1\text{ m/s})$ and $K_{measured}$</td>
<td>16.2</td>
<td>1134.3</td>
<td>152.5</td>
</tr>
</tbody>
</table>

Figure 3.21: $F$ and $\gamma$ as a function of the porosity simulated by DPLS.
3.2. SECOND CHARACTERIZATION OF SNOW SAMPLES

Figure 3.22: Tortuosity of 5 different samples (one of each type) simulated by DPLS as a function of the Reynolds number. The sample types are the following: Sample 13: //, Sample 14: □□○, Sample 20: ∧∧, Sample 22: □□, Sample 27: ●●.

well as $\gamma$ (Figure 3.24) as a function of porosity. $F$ had an average anisotropy coefficient of 15.61 with a standard deviation of 49.42, and $\gamma$ had an average anisotropy coefficient of 40.58 and a standard deviation 100.6.

3.2.5 Discussion

The porosity from the 3D data shows small relative differences with the measurements (Figure 3.17), having almost all relative differences smaller than 10%. This accuracy can be supported by the fact that the experimental method of determining the density used by Arakawa [8], namely gravimetry, is simple and accurate. Contrarily, the large relative differences between the SSA determined by stereology and by two-point correlation (Figure 3.16) can be explained by the lack of precision of the stereological experimental method, which was a model-based and not a design-based method [12,151]. It assumed that the pores are spherical. The calculated values from the tomography are more reliable as they are based on the complete imaging of the 3D-surface.

The permeability $K$ simulated with DPLS compares well to the directly measured permeability by Arakawa [8]. Only the sample nr. 11 shows a particularly high difference (176%). For this sample, porosity and SSA showed relatively high difference (10% and 38%, respectively), but not high enough to reflect the value obtained for $K$. This difference can therefore be due
to an error either during the measurement process or during the meshing procedure. For the rest of the samples, the difference can be explained by the different errors resulting from both the measurement and the computation, but also from the difference in the equation used. The measured values \cite{8} were calculated using Equation (2.14) and assuming a Darcian velocity, but for which the conditions were not completely fulfilled, as will be discussed later.

To our knowledge, the only other work comparing simulated values of permeability to measured values on the same samples is the work of Courville et al. \cite{39}. For this study, 13 samples were used. Mean differences of 6.7\%, with a standard deviation of 29.2\% were obtained. However, the study of Courville et al. (2010) characterized firn samples, which have a lower porosity than snow and a less varying microstructure. As snow structure cannot be simply characterized by its density, the present study show that DPLS can accurately characterize complex snow microstructures.

The fact that $K$ decreases with an increasing SSA is physically consistent because increased SSA leads to increased pressure drop and, consequently, lower $K$. This is further supported by previous comparison to semi-empirical models \cite{217}. The range of values obtained for $K$ is consistent with the previous works on permeability \cite{30, 39, 217}. The model for $K$ (Equation (3.9) ) compares particularly well with the one of Calonne et al. \cite{30}:

$$K_{\text{Calonne}} = 3r_\text{e}^2 e^{-0.013\rho}$$  \hspace{1cm} (3.12)

It also shows similarities with the widely-applied Shimizu model \cite{170}:

$$K_{\text{Shimizu}} = 0.077d_\text{e}^2 e^{-0.0078\rho}$$  \hspace{1cm} (3.13)
where \( d_e = 2r_e \) is the equivalent sphere diameter of a grain. Note that parameterization was performed based on grain size for the purpose of comparison with previous studies \([2, 3, 30, 78, 170]\). Alternatively, parameterization could be performed based on pore diameter. To compare the different models, \( K \) is plotted vs the density in Figure 3.25. For a density higher than 350 kg/m\(^3\), all the models are close to the simulated values and show a straight line. However, below 350 kg/m\(^3\), the values are more scattered. At higher density, the snow samples show less difference in their microstructure, whereas at lower densities, samples with similar density can have different microstructures, leading to a different permeability. At these lower densities (below 350 kg/m\(^3\)), Shimizu’s model (Equation (3.13)) seems to be inaccurate, whereas the model presented in this study and the one of Calonne et al. \([30]\) (Equation (3.12)) show a better agreement. The model of Calonne et al. \([30]\) is also simulation-based, with the use of the lattice-Boltzmann model, which can explain the high similarity between the two models. On the other hand, the equivalent sphere diameter of Shimizu was determined by measuring the greatest extent of snow grains using a hand lens \([170]\). This can induce some imprecision in the results, which is not the case of the model by Calonne et al. \([30]\).

![Figure 3.25: Comparison of the different models for \( K \) and \( K \) simulated by DPLS, vs density.](image)

As can be seen on Figure 3.20, \( \Pi_{pg} \) does not depend linearly on \( Re \) and is well fit by Equation (2.18). The simulated values of \( K \) obtained by applying the linear Darcy’s law (Equation (2.14)) show that inertial effects must be taken into account even at relatively low velocities. A velocity of 0.1 m/s
is clearly out of range, as the values of $K$ are twice as large as the ones obtained with 0.05 m/s. $K$ calculated with a velocity of 0.05 m/s showed small differences to $K$ with a velocity of 0.001 m/s. However, these values were consistently lower, which shows the necessity of using the third-order correction of Darcy’s law, even at such a small velocity.

$K$ values obtained by Arakawa et al. [8] were measured with velocities in the order of 0.5 m/s, too high to stay into the linear domain. This shows the necessity of using the extended Darcy’s law (Equation (2.17)) already at 0.05 m/s. This deviation from linearity is due to inertial effects, becoming more important than the viscous effects with increasing Re [88]. Under natural wind conditions, a velocity high enough to cause viscous effects can take place [34]. Darcy’s approximation is therefore possibly not valid in snow, as its applicability is restricted to particularly low Re. In contrast, the extended Darcy’s law (Equation (2.17)) shows reasonable accuracy for the range of Re encountered in nature. This is particularly the case for snow types with a large pore size, contributing to a large Re. This limitation should also be considered for the experimental measurements of snow, where the entering flow can easily be too high. In Hardy and Albert [65], the maximum velocity for which the linear Darcy’s law (Equation (2.14)) is still valid was estimated to be 0.056 m/s, whereas in Shimizu [170], the limit was set to 0.047 m/s. However, according to the previous calculations, both are still in the weak inertia regime. Note that the change of regime depends on Re, and not only on the velocity.

$F$ increases with SSA due to the inertial effects, an opposite tendency than $K$, as already observed previously [217]. Both $F$ and $\gamma$ tend to have generally an opposite tendency than $K$, as can be seen in Figures 3.20 and 3.24.

In Figure 3.22, the variation of tortuosity with Re is clearly visible. It supports the hypothesis of increasing inertial effects in comparison to viscous effects. Therefore, the tortuosity should not be seen as an intrinsic property of the material, but rather as a property dependent on the velocity of the fluid entering the snow. Tortuosity has been shown to be a powerful concept to describe diffusion in snow and in porous media in general [48,139].

One can observe a smaller difference in $K$ for samples with a smaller porosity. However, this cannot be observed for $F$ and $\gamma$. $A(K)$ and $A(F)$ are similar for most of the samples, except three of them. $A(\gamma)$ also shows similar results to $A(\gamma)$, except for a few samples giving particularly high values of $A(\gamma)$. The range of $A(K)$ is similar to the one observed by Calonne [30]. Sturm and Johnson [188] have shown that convective cells can form in a subarctic shallow snowcover, with air flowing in horizontal and vertical directions. In addition, ventilation by wind causes vertical and horizontal air flows [127]. Therefore, the determination of $K$, $F$ and $\gamma$ in both principal orientations of
the snow is essential to fully describe the airflow in snow.

### 3.2.6 Conclusion

The 3D geometrical representation of 34 samples of snow was obtained by sublimation tomography. Two-point correlation functions and the finite-element method were applied in DPLS for determining their morphological and mass transport properties. A direct comparison of permeability calculated by DPLS to the measured values showed a good agreement. A model was developed to determine permeability, Dupuit–Forchheimer coefficient and the third order correction of Darcy’s law as a function of the grain radius and the density. The extension of Darcy’s law indicated the importance of the inertial effects, which were present at low Reynolds numbers but were not taken into account in previous reports of permeability. The two-point correlation function allowed the determination of the specific surface area with more precision than the model-based stereological method. Anisotropy was observed in the three coefficients of the extended Darcy’s law, and the anisotropy coefficients for permeability gave a range consistent with the literature.
Chapter 4

Bone Tissue engineering\(^1\)

4.1 Introduction

The present study takes two basic constituents of a tissue culture and how they are influenced by each other into account: 3D scaffolds in a controlled fluid dynamic environment using a perfusion bioreactor. Two 3D scaffold types, exemplified here with two commonly used scaffold materials and geometries, are investigated. One represents a rather regular pore geometry of a polycaprolactone (PCL) scaffold generated by free-form fabrication \([24]\). The second type of scaffold is a silk fibroin (SF) scaffold manufactured with the salt leaching method and has a fairly irregular network of interconnected pores \([76, 124, 194, 198]\). Scaffold pore diameter, porosity and pore interconnectivity have a direct influence on the cellular behavior and the mechanical stimuli cells feel. To mimic healthy or diseased shear stresses in an in vitro model of healthy or diseased tissue such as for example bone with a perfusion bioreactor, it is important to know the mechanical stimuli a cell experiences at a given flow rate in a certain location in the 3D volume of a scaffold.

Another important aspect examined in the present work is the application of mechanical stimulation through fluid flow with a perfusion bioreactor. In tissue engineering studies with flow perfusion bioreactors, the mechanical input is usually generated through the adaptation of the flow rate at the pump connected to the system. More important is the knowledge of the flow rate within the porous scaffold and the corresponding shear stresses exerted on cells attached to the scaffold surface. Evidently, the geometry of the reactor and of the scaffold has a great influence.

In most CFD studies using μCT-based scaffold geometries, only subvolumes are evaluated due to computational limitations \([33, 83]\). It could

\(^1\)Material from this chapter has been submitted for publication in: E. Zermatten, J. R. Vetsch, D. Ruffoni, S. Hofmann, R. Müller and A. Steinfeld, Micro-computed tomography based computational fluid dynamics for the determination of shear stresses in scaffolds within a perfusion bioreactor. *Annals of Biomedical Engineering*, submitted, 2013.
be shown that the size of the sub-volumes can result in up to 30% difference in wall shear stress (WSS, $\tau_w$) values. The differences between WSS of different sub-volumes arise because small volume do not account for the scaffold heterogeneity. To avoid these differences the minimal model size should be at least 8-10 times the average pore diameter [106]. Other simulations in the context of properties of porous materials, propose a minimal representative elementary volume (REV) size of at least 3.5 and up to 14 times the average pore diameter [137,217]. To determine the pressure drop in a porous material the size should be chosen even bigger [217]. DPLS can be used in the field of tissue engineering, providing an accurate description of any porous structure than can be used as a scaffold.

The aim of this study is to determine the magnitude of $\tau_w$ acting on cells seeded on a surface of two types of porous 3D scaffolds in a perfusion bioreactor. The cellular mechanical environment is studied with the help of $\mu$CT based numerical simulations of the scaffold in combination with the bioreactor environment. Additionally, the level of WSS for each potential cell location on the scaffold is calculated. Fluid flow through the scaffold placed in a perfusion bioreactor is simulated by DPLS. Precise $\tau_w$ values are extracted to determine the mechanical stimulation cells experience when subjected to perfusion flow. Knowing the $\tau_w$ values for each cell location on the scaffold surface, it can be possible in the future to give recommendations for input flow velocities for the simulated scaffold. To our knowledge, modeling $\tau_w$ in a perfusion system including a whole scaffold has not been studied so far. Simulating the whole system will provide more information of the flow in the bioreactor and the influence of the flow field on the shear stress distribution in the scaffold.

4.2 Materials and Methods

4.2.1 Scaffolds and perfusion bioreactor system

Two scaffold types with different microarchitectures were considered: regular polycaprolactone (PCL) scaffold and an irregular silk fibroin (SF) scaffold. Both scaffolds have 10 mm-diameter, 3mm-length cylindrical shape. Figure 4.1 shows the 3D rendering of the $\mu$CT scans of the two scaffold types: (top left) PCL scaffold and (top right) SF scaffold. The scaffold pore diameter distributions obtained by morphological operations are shown in Figure 4.1(bottom).

The PCL scaffold was purchased from 3D Biotek [24]. According to the manufacturer, it has a nominal fiber diameter and fiber spacing of 300 $\mu$m.

The SF scaffold was produced as reported [124]. Cocoons from the silk-worm Bombyx mori L. were boiled in 0.02M Na$_2$ CO$_3$ for 2 h, purified in
Figure 4.1: μCT pictures of the two scaffold types, both with dimensions of 8 mm in diameter and 3 mm in length. (top left) free-form fabricated Poly-caprolactone (PCL) scaffold (top right) silk fibroin (SF) scaffold. (bottom) Scaffold pore diameter distributions.
ultrapure water and dried. The dried silk was dissolved in 9M LiBr solution (55 °C, 1 h), dialyzed, filtered and frozen at -80 °C overnight. The frozen solution was freeze-dried and dissolved in 1,1,1,3,3,3-hexafluoro-2-propanol. Subsequently, 1 ml of the solution was mixed with 2.5 g NaCl granules (diameters 224-315 µm) and the organic solvent was then allowed to evaporate. β-sheet formation of SF was induced by immersion into 90% MeOH [193]. NaCl was extracted and the SF scaffolds were dried at room temperature.

Both scaffolds were introduced inside a home-made perfusion bioreactor compatible for µCT imaging, as schematically shown in Figure 4.2. The perfusion system consists of three major parts: (1) a bioreactor housing, (2) bag containing the culture medium, and (3) a peristaltic pump (Figure 4.2A). The bioreactor housing (Figure 4.2B) can be equipped with different inlays, allowing the use of scaffolds with different dimensions and materials. Scaffolds are press-fit into the inlay to ensure a confined setting and directing the fluid flow through the scaffold. The bioreactor was designed such that the housing can be decoupled from the rest of the perfusion system to perform µCT scans. This system was successfully applied for perfusion studies using cell-seeded SF scaffolds [199].

Figure 4.2: Schematic overview of bioreactor system. (A) The bioreactor system contains three major parts: (1) The housing, (2) the media bag and (3) the pump. (B) CAD drawing of the bioreactor geometry used for the simulations: (1) bioreactor housing top, (2) bioreactor housing bottom, (3) inlay holding the (4) scaffold. Depending on scaffold material properties and size different inlays can be used to hold the scaffold in place. The flow direction is indicated by arrows.
4.2.2 Micro-computed tomography (µCT)

The 3D microarchitecture of the two scaffolds was acquired non-destructively by µCT measurements. Both scaffolds were measured in dry state using a desktop µCT [161] operated at 45 kVp and 177 µA. An integration time of 200 ms and frame averaging of 4 were used, resulting in a total scanning time of approximately 2.4 hours per sample. The reconstructed scans had a nominal isotropic resolution of 10 µm. After image reconstruction, a 3D Gaussian filter (SF: sigma=0.8 and support=1; PCL: sigma=1.2 and support=1) was applied to reduce the noise. The µCT data were then binarized using a global threshold corresponding to 4% and 4.5% of the maximum gray level for SF and PCL, respectively. Additionally, sharp features that were present in the SF scaffold due to the drying process were smoothed through applying a Gaussian filter with sigma=1 and support=2 which reduced the local surface curvature. The scaffolds were then rescaled to a resolution of 20 µm and virtually cut to a cylinder of 8 mm in diameter and 3 mm in length. This size corresponded to the size of the bioreactor inlay and for in vitro culture, scaffolds would be cut to these dimensions to fit into the bioreactor. Morphometric analysis was performed for both scaffolds to characterize pore diameter distribution [195].

4.2.3 Mesh generation and sensitivity analysis

The CFD domain is shown in Figure 4.2(B) and consisted of the whole bioreactor containing the scaffold. An in-house tetrahedron-based mesh generator [55] was used to create a computational grid directly from the digitalized geometry of the scaffold-bioreactor system (Figure 4.3). The mesh generator first covered the entire domain with large tetrahedrons (initial edge length of 0.375 mm), which were then gradually reduced in size according to a refinement process, followed by vertex rounding, cutting and smoothing. Such procedure resulted in a highly refined mesh on small features (e.g., struts inside the scaffolds, Figure 4.3B), and a coarser mesh far from the boundaries and for bigger features (e.g., bioreactor housing, Figure 4.3C). A mesh sensitivity study was carried out to determine the influence of the number of refinements on the simulation outcomes. Specifically, the number of mesh refinements was fixed ($N = 2$) for the bioreactor whereas for the scaffolds it varied from 2 to 5.

4.2.4 Computational fluid dynamics (CFD) simulations

The commercial CFD code ANSYS [7], based on the finite volume technique, was used to solve the 3D Navier-Stokes equations. The computational domain (Figure 4.3) consisted of the whole bioreactor with the scaffold. The boundary conditions were, at inlet, a uniform flow velocity with a flat profile
and, at outlet, a constant pressure of 1 atm. No-slip boundary conditions were applied at the solid-fluid interface. Three different inlet flow rates were simulated, corresponding to the minimum (0.1 ml/min), average (0.2 ml/min) and maximum (0.3 ml/min) flow rates obtained with a standard laboratory pump. The culture medium was described as a homogeneous and incompressible Newtonian fluid, having a density of 997 kg/m$^3$ and a dynamic viscosity of $8.9 \cdot 10^{-4}$ kg/(m·s). The temperature of the culture medium was set to 37°C representing body temperature. Main simulation outcomes were the flow velocity and WSS ($\tau_w$). The frequency distributions of $\tau_w$ were measured within 5 different regions of interest (ROI) along the scaffold length. Each region has a thickness of 600 µm to be representative of that location. The selected ROI did not include a small zone at the scaffold-bioreactor interface having a thickness of 100 µm and 140 µm for SF and PCL, respectively. These regions were excluded to avoid the influence of boundary artifacts.

4.3 Results

4.3.1 Micro-computed tomography (µCT)

The µCT scans confirmed the regular structure of the PCL scaffold (Figure 4.1(top left)) and the irregular structure of the SF scaffold (Figure 4.1(top right)). The two scaffolds had different pore diameter distributions (Figure 4.1(bottom)): For the PCL scaffold, the distribution was fairly asymmetric, peaked around 0.26 mm with a mean pore diameter of $0.22 \pm 0.06$ mm. For the SF scaffold, the distribution was bell-shaped, with a peak around 0.14 mm and a mean pore diameter of $0.16 \pm 0.08$ mm. The porosity of PCL and SF scaffolds were 37.91% and 55.48%, respectively.

4.3.2 Mesh sensitivity analysis

Table 4.1 shows the results of the mesh sensitivity analysis. For each simulation, the number of refinements within the scaffold was increased, leading to smaller mesh elements. Mesh convergence was assessed by computing the relative difference between two consecutive refinements in mean WSS and mean flow velocity. These two output parameters showed a quick convergence for the PCL scaffold with relative differences between refinements 5 and 4 less than 2.5% for mean $\tau_w$ and 1% for mean flow velocity. The simulations also converged well for the SF scaffold where the relative difference between the highest refined mesh (i.e., 5 refinements) and the one with 4 refinements was 11% and 2.2% for mean $\tau_w$ and mean flow velocity, respectively. Based on those trends, meshes with 5 refinements were used under the assumption that
Figure 4.3: Computational domain: (left) Bioreactor containing the scaffold. The bioreactor (right top) itself is meshed with a coarse grid (smallest element size before rounding, cutting and smoothing: $93.8 \, \mu m$), whereas the scaffold grid (right bottom) is finer (smallest element size before rounding, cutting and smoothing: $11.7 \, \mu m$)
introducing more refinements (which would be very costly from a computational viewpoint) would influence the simulation outcomes only less than 10%. The resulting CFD models of the PCL scaffold had 59 million elements and 115 million elements were used for the SF scaffold. Considering the element diameter, defined as the longest length of an element in the mesh, the minimum size of both meshes was about 12 µm, corresponding to approximately half of the voxel size. The average element diameter was 22.86 µm and 21.55 µm for PCL and SF, respectively. The distribution of mesh element sizes is shown in Figure 4.4. Their distribution was similar; however, the SF contained more highly refined elements and fewer bigger elements than the PCL scaffold.

Table 4.1: Mesh sensitivity analysis of the SF and the PCL scaffold. For each number of refinements, the minimum size of the mesh elements, the number of elements and the relative difference of WSS and velocity with the highest refined mesh is given.

<table>
<thead>
<tr>
<th># refinement</th>
<th>Min size [µm]</th>
<th># elements</th>
<th>%Δτw</th>
<th>%Δ velocity</th>
</tr>
</thead>
<tbody>
<tr>
<td>SF</td>
<td>2</td>
<td>93.8</td>
<td>5.11 \times 10^5</td>
<td>77.0</td>
</tr>
<tr>
<td></td>
<td>3</td>
<td>46.9</td>
<td>3.92 \times 10^6</td>
<td>43.4</td>
</tr>
<tr>
<td></td>
<td>4</td>
<td>23.4</td>
<td>2.33 \times 10^7</td>
<td>10.9</td>
</tr>
<tr>
<td></td>
<td>5</td>
<td>11.7</td>
<td>1.13 \times 10^8</td>
<td>-</td>
</tr>
<tr>
<td>PCL</td>
<td>2</td>
<td>93.8</td>
<td>3.68 \times 10^5</td>
<td>52.1</td>
</tr>
<tr>
<td></td>
<td>3</td>
<td>46.9</td>
<td>2.46 \times 10^6</td>
<td>17.1</td>
</tr>
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<td></td>
<td>4</td>
<td>23.4</td>
<td>1.20 \times 10^7</td>
<td>2.5</td>
</tr>
<tr>
<td></td>
<td>5</td>
<td>11.7</td>
<td>5.58 \times 10^7</td>
<td>-</td>
</tr>
</tbody>
</table>

4.3.3 CFD simulations

The frequency distributions of τ_w at an average flow rate of 0.2 ml/min for both scaffold geometries are shown in Figure 4.5. The PCL scaffold showed quite different WSS distributions depending on the location along the scaffold: the WSS distribution shifted toward higher values from the entrance of the fluid flow (region 1, Figure 4.5(bottom left)) to the exit location (region 5, Figure 4.5(bottom left)). It became broader, indicating a higher heterogeneity of WSS in the regions 4 and 5. Moreover, the distributions relative to regions 2 to 5 showed a pronounced asymmetric peak with a flat plateau, the plateau being particularly flat in the regions 4 and 5. The simulation of the SF scaffold showed a different behavior characterized by identical τ_w distributions along the length of the scaffold, with exception of the entrance location (region 1, Figure 4.5(bottom right)), which showed a similar behavior than for the PCL
4.3. RESULTS

The mesh element diameter is defined as the longest length of the mesh element.

scaffold. After a short travel distance through the scaffold, shear stresses were homogenous throughout the whole scaffold volume.

In practice, inlet flow rates can be adjusted through an external pump. The effect of inlet flow rates from 0.1 ml/min to 0.3 ml/min on the mean $\tau_w$ in both scaffold types is shown in Figure 4.6. For both scaffolds, a monotonically increasing linear correlation was obtained, resulting in higher shear stresses at higher flow rates. Shear stresses were minimal in the regions where the fluid gets first contact with the scaffold (region 1) and increased towards downstream regions (regions 2-5). The slope of the lines in the 5 regions was dependent on the location along the scaffold (Figure 4.6). In accordance with the frequency distributions, the mean WSS values were similar between regions 2 and 3 and between regions 4 and 5 for the PCL scaffold, defining three distinct regions over the scaffold volume. In contrast, the mean WSS in regions 2, 3, 4 and 5 were almost identical for the SF scaffold, defining two regions, one at the inlet and one throughout the rest of the scaffold. The histogram of WSS for different velocities is shown in Figure 4.7 for PCL and in Figure 4.8 for SF. An increasing inlet velocity led to an increase of the frequency of high WSS. For PCL, in regions 3 and 5, increasing the inlet velocity to 0.3 ml/min led to a plateau in the histogram, i.e. an almost constant frequency of WSS between 0.001 and 0.004 Pa. For SF, in regions 3 and 5, an increase of velocity reduced the slope of the frequency distribution,
Figure 4.5: Schematic view of the 5 regions of interest in the scaffold (top). WSS frequency in 5 different slices of the scaffolds, perpendicular to the flow, from entry to exit, in PCL (bottom left) and SF (bottom right) scaffolds, respectively. Inlet velocity is 0.2 ml/min.
however without attaining a plateau.

The 3D fluid flow streamlines across both scaffolds is shown in Figure 4.9. The flow direction is from top to bottom. The scaffold is represented semi-transparent for a better visualization. The streamlines in the PCL showed a rather regular behavior, while those in the SF scaffold were more random.

### 4.4 Discussion

The goal of this study was to determine the WSS acting on the surfaces of two scaffold types commonly used in tissue engineering applications, a 3D printed one with a regular pore geometry (PCL) and one obtained through a salt leaching process resulting in a rather irregular distribution of pores (SF).
Figure 4.7: WSS frequency in PCL for an inlet velocity of 0.1, 0.2 and 0.3 ml/min, for region 1 (top left), region 3 (top right) and region 5 (bottom).
4.4. DISCUSSION

Figure 4.8: WSS frequency in SF for an inlet velocity of 0.1, 0.2 and 0.3 ml/min, for region 1 (top left), region 3 (top right) and region 5 (bottom).
Figure 4.9: Fluid flow through (left) PCL and (right) SF scaffold. The scaffolds are vertically cut in the middle to visualize only a subregion. Perfusion flow is simulated top to bottom and the lines represent the streamlines through the sample. The horizontal edge length is 2 mm for both scaffolds.
4.4. DISCUSSION

\( \mu \)CT scans of the two different scaffolds were used in finite volume simulations to model the flow through the pores and the entire scaffold-bioreactor system was taken into account in the model.

4.4.1 Micro-computed tomography (\( \mu \)CT)

\( \mu \)CT was shown to be a suitable non-destructive technique to extract 3D morphological parameters of scaffolds for subsequent finite element simulations [75]. As polymeric scaffolds need to be scanned in their dry state in order to provide enough x-ray contrast, edged features were present especially in the SF scaffold where very fine structures close to the resolution limit were present. In an in vitro culture, these scaffolds are hydrated by their surrounding aqueous environment which would result in a smoother surface structure, as can be seen in histological sections of hydrated scaffolds (data not shown). Consequently, a second smoothing procedure was applied to the SF scaffolds to reduce their local surface curvature. This reduction was more effective in regions where the surface curvature was high and represented the swelling of the scaffold in the wet state by decreasing its porosity by about 12%.

4.4.2 Mesh sensitivity analysis

The mesh refinement study indicated the need of a highly refined mesh especially for the SF scaffold. The refinement of the PCL converged more rapidly than the refinement of the SF, and therefore less mesh cells needed to be refined at the last step, as can be seen in Figure 4.4: the PCL histogram showed fewer small elements on the first peak than SF and more elements on the second peak. This is reflected in Table 4.1 where less mesh cells were refined after the 4th refinement in the PCL scaffold, attributed to the larger and more regular pores in the PCL scaffold compared to those in the SF scaffold.

At the highest mesh refinement (5 refinements) the smallest mesh element length was 11.7 \( \mu \)m for both scaffolds, being already smaller than the resolution of the \( \mu \)CT scan (20 \( \mu \)m). With relative differences smaller than 11% for WSS and smaller than 2.2% for flow velocity, 5 refinements were considered sufficient for the present study.

4.4.3 Computational fluid dynamics (CFD) simulations

Flow velocity and WSS in an entire scaffold-bioreactor system was simulated. This setup mimics the geometrical boundary conditions that have been applied for preliminary cell experiments [199]. Modeling not only the scaffold but the scaffold and the bioreactor housing takes into account that the inlet
flow is guided by the geometry of the bioreactor. The simulated scaffold volume was bigger than the representative elementary volume (REV), defined as the smallest cubic volume to be considered as a continuum in a porous medium. Choosing a volume smaller than the REV would affect the obtained WSS considerably and reduce the precision of the results [196]. Additionally, lateral boundary conditions would influence simulation results up to 30% when modeling only a small part of the scaffold [33, 106]. The diameter and length of the PCL scaffold were 36 and 13 times larger than the mean pore diameter (0.22 ± 0.06 mm), whereas for the SF scaffold the diameter and length were 50 and 19 times larger than the mean pore diameter (0.16 ± 0.08 mm), respectively. The dimensions of both scaffolds were therefore larger than the suggested minimum REV, which is reported to be between 2 times [106] up to about 14 times the mean pore diameter [217]. The REV is even larger for the determination of pressure drop [67, 217]. Furthermore, it has also been shown that the length of the sample parallel to the flow direction can be chosen 2 to 3 times shorter than the perpendicular length without affecting the precision of the results [217].

Both scaffolds showed a similar WSS behavior at the entrance region (region 1), since the pore geometry only starts having an impact on the flow at this point (Figure 4.5). On the other hand, the scaffold microarchitecture had a strong influence on the WSS distribution in downstream regions (region 2-5). In the SF scaffold, the WSS achieved its maximum already in region 2 and stayed constant until the exit region (region 5), whereas that was not the case for the PCL scaffold that displayed two distinct phases from region 1, namely regions 2-3 and regions 4-5. The smaller and irregular pores of the SF scaffold seemed to condition the flow more rapidly than the bigger pores of the PCL scaffold.

The behavior of WSS in the PCL scaffold showed a related trend in every region, with the number of mesh cells feeling a low WSS increasing to attain a peak, before decreasing again. The channel-like geometry and the larger pore diameters of the PCL could explain this behavior. The peak was slightly shifted to the right as the inlet flow velocity increases, as can be seen from Figure 4.7. This peak behavior was comparable to other computational studies [33, 116, 160]. However, the WSS in the SF scaffold did not show a similar behavior in regions 2 to 5; the SF was showing a high amount of very low WSS before the counts decreased rapidly with increasing WSS without showing any peaks or shoulders. Increasing the entrance flow rate increased WSS through the scaffold linearly, as expected for a laminar regime with Reynolds number maintained below 0.4, in accordance with other studies [33, 97, 116].

Our results were close to values obtained by other groups, although direct comparisons cannot be made due to different applied geometries and/or boundary conditions and/or missing descriptions. In our study, an entrance
flow rate of 0.2 ml/min (corresponding to a flow velocity of 0.066 mm/s) resulted in a mean WSS of 3.08 mPa and of 3.68 mPa in the middle region (region 3) for PCL and SF scaffolds, respectively. Simulating a regular scaffold with a shape comparable to the PCL scaffold used in this study, Lesman et al. [97] obtained a WSS of 11 mPa for an entrance flow velocity of 0.105 mm/s with a pore size of 0.15 mm. Since WSS is proportional to the entrance flow velocity, the assumption can be made that for an entrance flow velocity of 0.066 mm/s, Lesman et al. would have obtained a WSS of about 6.9 mPa, which is twice the value obtained by our simulations. The smaller pore size the scaffold used in the study however can explain the bigger WSS value [33,97,116].

Van Ransbeeck et al. [196] reported WSS ranging from 1.1 to 1.95 mPa with an inlet flow velocity of 0.034 mm/s for irregular scaffolds with a porosity of 70% and a mean pore size of 0.275 mm. Cioffi et al. [33] obtained average WSS between 3.28 and 3.94 mPa, with an inlet flow of 0.053 mm/s, for an irregular scaffold of 77% porosity. Maes et al. [106] studied two different scaffolds, an irregular hydroxyapatite (73% porosity, 0.27 mm pore size) and a titanium one (77% porosity, 0.28 mm pore size), and obtained average WSS of 1.46 and 1.95 mPa, respectively, both with an inlet flow velocity of 0.034 mm/s. The calculated mean WSS of 3.68 mPa for the SF scaffold was comparable to the values observed in the aforementioned studies. However, one has to be careful when comparing those results, because of the different scaffold geometry as well as the different bioreactor used. Moreover, the aforementioned studies were simulating the scaffold itself, or only a part of it. This can lead to unprecision due to a scaffold smaller than the REV and due to the fact that the bioreactor itself was not taken into account in the simulation.

Shear stresses acting on cells seeded onto 3D scaffolds have been shown having an influence on cell viability, proliferation and gene regulation [143]. Mean surface shear stresses of $5 \cdot 10^5$ Pa as calculated with the Lattice-Boltzmann method with no correction factor correlated to the highest cell viability and proliferation at a flow rate of 0.01 ml/min [143]. Their study used a coarse resolution of 68 µm for their simulations. With this method, the lattice elements were all the same size, which could induce a lack of precision on small features when using too big elements, or too many useless elements on big features when using smaller elements, which can increase the computational time consequently.

In the future, experimental validation will be needed to reveal whether cells encountering similar shear stresses do react similarly in terms of cell proliferation, differentiation or extracellular matrix production by means of longitudinal monitoring techniques. As a general limitation it needs to be taken into account that it mustn’t only be the shear stresses that influence cell
behavior. Other mechanisms such as increased mass transport through the scaffold volume or flow streaming potentials can stimulate cells and may not be clearly differentiated from the effect of shear stress in a 3D environment.

Another limitation of the current manuscript is that it did not take into account the volume of the seeded cells nor the volume of the extracellular matrix (ECM) produced by the cells. Our study solved the situation before cell seeding. After seeding, the cells fill up the spaces within the pores and, over time, they would surround themselves with ECM. This continuous obstruction of the pores would result in different WSS acting on the cells due to two reasons: i) the decreased porosity and ii) the cells might no longer be located at the scaffold surface but be protected or shielded by their own ECM. To distinguish these time-dependent phenomena from each other and draw conclusions on how mechanical input is transmitted to the cells, more advanced 3D monitoring and simulation techniques will be needed in the future.

The PCL scaffold with a regular pore geometry gave rise to a peak in WSS. By controlling the scaffold architecture (porosity, pore size, etc.) in the manufacturing process, it should be possible to generate ranges of WSS that promote a certain type of tissue formation [89, 113, 131, 159]. In Lesman et al. [97], when reducing the pore size of a regular scaffold to take the cell growth into account, an increase of the shear stress was observed. In a scaffold with an irregular pore size and geometry distribution, the flow seems to choose some preferable channel as can be seen in Figure 4.9B, and it would become even more difficult to predict the forces cells are subjected to. From this point of view, in order to be able to tune the mechanical load for studies for the elucidation of how the mechanical environment regulates cell behavior, a regular scaffold seemed more promising.

With this manuscript we provide a method to simulate the WSS acting on the surface of two types of commonly applied scaffolds in tissue engineering by taking both the scaffold as well as the geometrical environment provided by the bioreactor into account. We provide insight into what cells seeded onto the surface of such scaffolds might sense in terms of mechanical loading at various locations throughout the scaffold volume. If tissue engineers want to be able to control and predict cell behavior in order to generate tissues in vitro, it will be of great interest to correlate cell behavior in a defined location in a scaffold with the mechanical load these cells are subjected to. This study enables to predict for each potential cell location within the scaffold the WSS level a cell seeded into this position will experience. Correlating this input parameter with experimental output data will broaden our insight into how mechanical loads will affect tissue development in vitro. The herein proposed method also enables new scaffold designs to be adjusted to a certain shear stress level for the cells before a scaffold is being subjected to costly in vitro experiments.
Chapter 5

Ceria reticulated porous ceramics

5.1 Introduction

Cerium oxide (ceria, CeO$_2$) has emerged as a highly attractive material choice for the two-step H$_2$O/CO$_2$ splitting solar thermochemical cycle based on redox reactions [32], represented by:

High-T reduction:

$$\text{CeO}_{2-\delta} \xrightarrow{\Delta H} \text{CeO}_{2-\delta-x} + \frac{x}{2}\text{O}_2 \quad (5.1)$$

Low T-oxidation with H$_2$O:

$$\text{CeO}_{2-\delta-x} + x\text{H}_2\text{O} \rightarrow \text{CeO}_{2-\delta} + x\text{H}_2 \quad (5.2)$$

Low T-oxidation with CO$_2$:

$$\text{CeO}_{2-\delta-x} + x\text{CO}_2 \rightarrow \text{CeO}_{2-\delta} + x\text{CO} \quad (5.3)$$

The first step proceeds via the thermal decomposition of CeO$_2$, usually to a non-stoichiometric state, and O$_2$ is evolved. The reduced ceria is then re-oxidized in the second lower temperature step using steam or CO$_2$ to produce H$_2$, CO, or a synthesis gas mixture (CO and H$_2$). The only net inputs are solar energy, water, and CO$_2$. The net reactions are H$_2$O = H$_2$ + 1/2O$_2$ and/or CO$_2$ = CO + 1/2O$_2$, and O$_2$ and H$_2$/CO are released in separate steps, thereby eliminating the need for high-temperature gas separation. The syngas mixture H$_2$/CO can be further processed to liquid hydrocarbon fuels (via Fischer-Tropsch and other catalytic processes), such as diesel, kerosene,

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1Material from this chapter has been extracted from the semester project of Silvan Suter, entitled Tomography-based determination of radiative heat transfer properties of a reticulate porous ceramic made of ceria, January 2012. This project was directly supervised by E. Zermatten.
methanol, and gasoline using existing conventional technologies. This ther-
mochemical cycle has been demonstrated using a solar reactor [32]. Reticulate porous ceramics (RPC) exhibit favorable heat and mass transfer character-
istics for high-temperature solar thermal and thermochemical reactors [126].
The knowledge of their properties is crucial for their optimal design and op-
eration. The RPC structure of ceria used in this study, depicted in Figure 5.1, has been developed in collaboration with the Swiss Federal Laboratory for Material Science and Technology (EMPA).

The RPC structure is developed to offer a high permeability to radiation gases and a high mechanical stability [119]. Its large pores, in comparison to a felt which was previously used, allows an efficient light penetration, leading to a homogeneous temperature profile across the material [108]. Its lower porosity permits a higher mass loading in the reactor, leading to more oxygen re-
lease [108]. The structure has been produced by the Schwartzwalder Replica Method [165], which consists of coating a 8-10 ppi foam out of polyurethane with a slurry composed mainly of ceria powder and ZrO$_2$, and finally sintering the foam at high temperature [119].

To optimize the H$_2$O/CO$_2$ splitting process, the radiation properties of the ceria RPC are determined. A collision-based Monte Carlo (MC) method is used on a 3D digital representation of the RPC to determine its extinction coefficient and scattering phase function. Spectroscopy measurements are carried out to validate the numerically determined extinction coefficient.

5.1.1 Methodology

Computer tomography

The data was obtained by CT performed at EMPA. The scan parameters are listed in table 5.1. A $20 \times 20 \times 36$ mm$^3$ cuboid ceria sample is scanned. Figure 5.2 shows the 2D and 3D rendering of the scanned sample obtained by CT. For the simulations, a subset of the scanned sample of $510 \times 510 \times 510$ voxels is used. The digital images are first converted from 16 bit integers to 8 bit. A threshold value is defined by the mode method to determine the phase boundary. A cross section of the ceria sample after segmentation is shown in Figure 5.3.

MC method

The Monte Carlo ray tracing method described in Section 2.13 is used to determine the extinction coefficient $\beta$ and scattering phase function $\Phi$ of the ceria RPC.

The following assumptions are made:
Figure 5.1: Schematic of a solar reactor for the two step thermochemical syngas production with a RPC absorber made of ceria [32,56,57]
Table 5.1: Scan parameters for tomography performed at EMPA.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>acceleration voltage</td>
<td>220 keV</td>
</tr>
<tr>
<td>beam current</td>
<td>45 µA</td>
</tr>
<tr>
<td>photon energy</td>
<td>~150 keV</td>
</tr>
<tr>
<td>no. of projections</td>
<td>721</td>
</tr>
<tr>
<td>exposure time per projection</td>
<td>6272 ms</td>
</tr>
<tr>
<td>distance object source</td>
<td>102.3 mm</td>
</tr>
<tr>
<td>distance detector source</td>
<td>1145 mm</td>
</tr>
<tr>
<td>focal spot size</td>
<td>~7 mm</td>
</tr>
<tr>
<td>size of detector cells</td>
<td>400 × 400 µm²</td>
</tr>
<tr>
<td>size of detector array</td>
<td>1024 × 1024 pixel</td>
</tr>
<tr>
<td>voxel edge length</td>
<td>35.7 µm</td>
</tr>
</tbody>
</table>

**Geometrical optics** Geometrical optics are valid for \[ \frac{\pi d}{\lambda} > 5 \] \hspace{1cm} (5.4)

Most of the solar radiation is comprised between wavelengths of \( \lambda = 300 \text{ nm} \) and 1900 nm. For a chemical reactor operating at 1500 K and 800 K, the peak radiation occurs at 1900 nm and 3600 nm, respectively [32]. The RPC pore size is of approximately 8 ppi, therefore \( d \) is of the order of the mm. The geometrical optics are thus valid.

**Homogeneity** Porosity calculations based on two-point correlation function are performed on subsequently growing volumes to determine the minimum REV for which the homogeneity assumption is valid. However, the RPC samples used for the spectroscopy measurements showed some inhomogeneities that might influence the results.

**Isotropy** A numerical experiment [134] is performed to investigate the isotropy of the RPC. Eight sub-volumes are subjected to a large number of parallel and uniformly distributed rays along the three Cartesian coordinates. Three directional extinction coefficients are determined and are within 12.91 % of each other. These results are shown in Section 5.2.2.

**Opaque solid** Ceria is assumed to be opaque [66]. However, according to Liang et al. [98], this assumption could be valid only for \( \lambda < 400 \text{ nm} \). Longer wavelengths would require a semi-transparent approach [69] and Bouguer’s law would not be valid. Here, ceria is assumed opaque also for longer wavelengths for simplicity.
5.1. INTRODUCTION

Figure 5.2: Horizontal cross section (left) and 3D rendering (right) of the ceria sample obtained by computed tomography

Transparent gas According to previous studies [67,137], the absorption coefficients of CO and H\textsubscript{2}O are of 0.77 and 2.63 m\textsuperscript{-1}, respectively, for incident solar radiation and gas temperature of 800 K and 10 bar pressure. Absorption coefficients are 26.1 and 40.2 m\textsuperscript{-1} for re-radiation from the reactor wall at 1100 K. These absorption coefficients are 10 to 10\textsuperscript{2} times lower than the value of the extinction coefficient presented in Section 5.2.2. The gas can therefore be assumed transparent and non-participating (\(\kappa_{\text{gas}} = \sigma_{\text{gas}} = 0\)).

The results for the scattering phase functions are compared to the following analytical solutions of the phase function for large, diffuse, opaque spheres [171]:

\[
\Phi_d(\mu_s) = \frac{8}{3\pi} \left( \sqrt{1 - \mu_s^2} - \mu_s \arccos \mu_s \right)
\]  

(5.5)

and large, specular, opaque spheres [171]:

\[
\Phi_s^\lambda(\mu_s) = \frac{\rho^\lambda \left( \sqrt{1 - \mu_s^2} \right)}{1 - \alpha^\lambda}
\]  

(5.6)

Spectroscopy measurements

Experimental measurements of the extinction coefficient are performed to validate the MC simulations. A spectroscopic system developed by Coray et al. [36, 37] in the radiation laboratory of PREC (RadLab) is used. The setup is depicted in Figure 5.4. The main hardware components are: (1) a dual Xe-arc/Cesiwid-glowbar lamp as a source of radiation, (2) a double
CHAPTER 5. CERIA RETICULATED POROUS CERAMICS

Figure 5.3: 2D visualisation of the tomography data after segmentation by the mode method.

Figure 5.4: Experimental spectroscopy setup [36, 37]: (1) dual Xe-arc/Cesiwid-glowbar lamp, (2) double monochromator, ((3) and (5)) collimating and focusing lens pairs, (4) sample, (6) detector on a rotary arm, (7) optical chopper, (8) lock-in amplifier, (9) PC data acquisition system.
monochromator (Acton Research Spectra Pro Monochromator SP-2355 series) with monochromator exit slit (20), (3) and (5) two imaging lens pairs (MgF$_2$, focal lengths $f = 75$ mm and $f = 150$ mm, (4) a sample, (6) a detector (Si/PC-HgCdTe sandwich with thermoelectric cooler) mounted on a rotary arm, (7) an optical chopper to modulate the radiation exiting the monochromator, (8) a lock-in amplifier to measure the modulated signal, and (9) a PC data acquisition system. With this setup, wavelengths from 0.3 $\mu$m to 4 $\mu$m can be measured, with a spectral resolution of $\pm 1$ nm. The maximum acceptance angle for detection of an incoming ray measured with respect to the optical axis is less than 4°. The transmittance of the RPC is measured for wavelengths of $\lambda = 350$ nm, 500 nm and 850 nm. Three different sample thicknesses are used: 20 mm, 18 mm and 12 mm. The transmittance is measured both at 0° and at various angles.

5.2 Results

5.2.1 REV

The length of the representative elementary volume $l_\text{REV}$ is determined based on porosity with an error band of $\xi = 0.05$. Unlike the determination of permeability, which needs larger REVs based on pressure drop, the determination of REV based on porosity is sufficient to determine the radiative properties. The resulting $l_\text{REV}$ is 5.68 mm.

5.2.2 Extinction Coefficient

MC method

$10^7$ rays ($N_r$) are emitted within a volume $V_0$ of edge length $l_0 = 6$ mm. The maximal path length is $s_{\text{max}} = 6.1$ mm. The radiation intensity decline of unextincted rays is given by Equation 2.26. The results are plotted in Figure 5.5 with a fit to Bouguer’s law (Equation (2.27)). The resulting extinction coefficient is of $\beta_{\text{MC}} = 278.74$ m$^{-1}$, with a RMS of 0.017 m$^{-1}$.

Spectroscopy Measurement

The transmittance measured by spectroscopy is approximately constant for the three different wavelengths used. The results are averaged for each sample thickness and plotted in Figure 5.6 along with the simulation results and a fit to Bouguer’s law for both the experimental and measured results. The extinction coefficient can be extracted from Bouguer’s law and is of
\[ \beta_{\text{ex}} = 299.31(+53.98; -36.45) \text{ m}^{-1}. \]

The uncertainty of the experimental measurement is also shown in Figure 5.6. The horizontal bars correspond to the uncertainty in the sample thickness, resulting from the difficulty to cut the RPC precisely. The vertical bars correspond to the uncertainty in the measured intensity, resulting from the small size of the incident ray compared to the pore size: the incident ray could be totally blocked at some positions of the sample, but penetrate through the RPC without hitting any material at other positions. The experimental and MC results show a good agreement. The differences could occur from the difference of technique; the MC method emits rays in all directions, whereas the spectroscopic system emits only rays from one direction. Moreover, the sample used in the measurements is not the same as the scanned one, even though both were produced with the same procedure.

**Directional Extinction Coefficient**

The extinction coefficient in the three directions of the sample are computed as described in Section 5.1.1, with a number of rays \( N_r = 10^5 \). The results are shown in Figure 5.7 and listed in Table 5.2. \( \beta_x, \beta_y \) and \( \beta_z \) show relative differences within 12.91 %, indicating either a slight anisotropy, or statistical errors in the simulations.
5.2. RESULTS

Figure 5.6: Intensity ratio with fit to Bouguer’s law, for MC method and spectroscopy measurements.

Figure 5.7: Intensity ratio $I/I_0$ along the three Cartesian axes.

Table 5.2: Mean extinction coefficient along the three Cartesian axes, with their RMS.

<table>
<thead>
<tr>
<th></th>
<th>x</th>
<th>y</th>
<th>z</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\beta_{MC} [m^{-1}]$</td>
<td>278.95</td>
<td>248.14</td>
<td>284.91</td>
</tr>
<tr>
<td>RMS</td>
<td>0.4399</td>
<td>0.4653</td>
<td>0.4354</td>
</tr>
</tbody>
</table>
5.2.3 Scattering Phase Function

MC method

The probability distributions of the incident and the scattered cosines are computed as described in Section 2.13. Figure 5.8 shows the probability distribution function of the incident cosines $F_i(\mu_i)$. The scattering phase function is calculated from the cosines of the scattered rays (Equation 2.30). It is plotted in Figure 5.9 for both specular and diffuse reflection, for a wavelength of $\lambda = 300$ nm and $\lambda = 800$ nm in the specular case. The results are compared to the analytical results of large diffuse and specular spheres. The specular cases computed for RPC is close to an isotropic scattering behavior. The result is slightly changing with the wavelength, since the reflectivity is obtained from Fresnel equation with wavelength dependent refractive indices. The result of the diffuse case is independent from the wavelength. The RPC shows slightly more backscattering than a large diffuse sphere.

Due the rough solid surface, diffuse reflection is expected. With this assumption, the scattering phase function is well approximated by (RMS = 0.00899):

$$\Phi_{\text{Diffuse}} = 0.5945\mu_s^2 - 1.4095\mu_s + 0.8018 \quad (5.7)$$

![Figure 5.8: Probability distribution function of the incident cosines $\mu_i$.](image1)

![Figure 5.9: Scattering phase functions for diffusely and specularly reflecting surfaces versus cosines of scattered rays $\mu_s$.](image2)

Angular Measurements

The angular intensity is also measured by spectroscopy for an angle varying between 10° and 150° and is shown in Figures 5.10 and 5.11. The intensity
drops between $0^\circ$ and $10^\circ$ by a factor of $10^2 - 10^4$ and increases again after $80^\circ$, showing predominant backscattering. A significant increase is observed for a wavelength of $\lambda = 850$ nm. The present measurements do not account directly for the scattering phase function, since the rays can experience more than one scattering event before exiting the sample. An inverse analysis [36] should be performed to determine the scattering phase function, which could be then directly compared to the computed one.

![Figure 5.10: Measured angular intensities for two wavelength: $\lambda = 350$nm and $\lambda = 500$nm](image1)

![Figure 5.11: Measured angular intensities for a higher wavelength of $\lambda = 850$nm](image2)

### 5.2.4 Convergence of MC method

A convergence study was carried out based on the relative error of the 2-norms of $G_s$ and $F_i$. The relative error was computed for number of rays of $N_r = 10^5$, $10^6$ and $10^7$ with a reference computation with $10^8$ rays. The convergence norms are

$$\epsilon_s = \frac{\|G_s - G_{s,\text{ref}}\|_2}{\|G_{s,\text{ref}}\|_2} \quad (5.8)$$

$$\epsilon_{\mu i} = \frac{\|F_i - F_{i,\text{ref}}\|_2}{\|F_{i,\text{ref}}\|_2} \quad (5.9)$$

The relative errors decreased with increasing number of rays and exhibited convergence. The results presented in this study were based on computations with $N_r = 10^7$ rays.
5.3 Conclusion

A MC ray tracing approach was applied directly on the exact 3D geometry of a ceria RPC obtained by CT. Its extinction coefficient $\beta$ and scattering phase function $F$ were determined and can be directly applied in volume averaged models for the design and optimization of thermochemical reactors. The extinction path length and scattering angle were determined for a large number of rays. The extinction coefficient obtained by MC was of 278.74 m$^{-1}$ and showed a good agreement with the experimental results measured by spectroscopy. Isotropy was assumed by comparing the directional extinction coefficients along the 3 Cartesian axes. The scattering phase function was computed for both specular and diffuse case, and were compared to the analytical solutions of large specular and diffuse spheres.
Chapter 6

Conclusions and outlook

In this thesis, the determination of porous media’s properties by tomography based DPLS was presented. The methodology, originally developed for the characterization of ceramic foams and packed beds for solar thermochemical applications, has been used successfully to other fields, namely snow and bone tissue regeneration.

6.1 Conclusions

In Chapter 3, the application to snow characterization was developed. A first study, in Section 3.1, characterized 5 representative snow samples by determining their permeability and Dupuit-Forchheimer coefficient. The methodology consisted of: i) obtaining the complex 3D geometrical representation of the snow microstructure by computer tomography directly on the snow samples. ii) The µCT scans were then digitalized and used in direct pore-level simulations (DPLS). iii) An in-house tetrahedron- based mesh generator was used to create the computational grid directly on the µCT data. iv) Mass and momentum conservation equations were numerically solved at the pore scale by the finite-volume method.

Pressure drop over the snow sample was determined and fitted to the Darcy’s law extended by the Dupuit-Forchheimer term (Equation (2.16)), allowing for the determination of $K$ and $F$. This extension to Darcy’s law gives the pressure drop as a 2nd order function of the velocity. This equation showed a good agreement with the data. $K$ and $F$ showed different behaviour depending on the snow types. The importance of the representative elementary volume was emphasized. It was observed that the determination of the REV based on porosity is not sufficient to determine accurately the pressure drop or velocity. For these quantities, larger REV were needed. The length of the sample parallel to the flow was chosen shorter than the two other lengths, without jeopardizing the precision of the results. The results were compared to analytical and semi-empirical models of porous media with a simplified
A model specially developed for snow was used, whereas for $F$ only general models for porous media were found. To our knowledge, no other study investigated the Dupuit–Forchheimer coefficient in snow. $K$ and $F$ were determined in the horizontal direction of the sample, to look at their anisotropy, which were dependent on the snow preparation. The methodology showed to accurately account for the complex snow microstructure. It demonstrated that morphological parameters such as porosity, pore or particle size are not sufficient to fully describe the material. These calculated effective transport properties can be applied in continuum models of snowpacks.

The second study on snow, developed in Section 3.2, characterized 34 different snow samples, from 5 different snow types. Those samples were previously characterized experimentally and casted with DMP for their conservation [8]. Their 3D geometrical representations were obtained by sublimation tomography, in which the negative of the sample is obtained by scanning the DMP casted in snow. Their porosity and specific surface area were determined by two-point correlation function. The 3rd order correction to Darcy’s law was used to determine $K$, $F$ and $\gamma$. To assess the precision of this law, different options were tested, using the 2nd order correction, the 3rd order correction and a combination of both for different Re. All of these laws yielded fits close to the data values, however the 3rd order correction (Equation 2.17) gave a slightly smaller NRMS. The results of permeability, porosity and specific surface area were compared to the experimental results obtained previously [8]. The results showed a good match, and permitted to assess the validity of DPLS in snow. The direct comparison between measurements and simulation on the exact same sample on snow is difficult, and only one previous study on firn was found to also use a direct comparison [39]. A model was given to determine $K$, $F$ and $\gamma$ as function of the grain radius and the density. This model was compared to other models on snow. The importance of the inertial effects was emphasized. In the snow field, no other study was found to take the inertial effects due to higher Re into account. The snow studies on permeability always simply use the non-extended Darcy’s law (Eq. 2.14) to characterize them. However, it was found that even at low Re (Re<1), the inertial effects are significant. This study completed our first study on snow, by showing the validity of DPLS on a large set of samples, and by allowing the direct comparison to measurements.

In Chapter 4, DPLS was applied to the characterization of porous scaffolds used in bone tissue engineering. Two different scaffolds of different materials and geometries were investigated. The first type was a polycaprolactone (PCL) with a regular geometry, whereas the second one was made of silk fibroin (SF), with a more random geometry. The scaffolds were scanned by $\mu$CT and meshed with the geometry of the bioreactor. The meshing of the
whole bioreactor provides a better insight on the flow field, without adding too many mesh elements, since the bioreactor itself was coarsely meshed. In the previous tomography-based studies in the field of bone tissue engineering, a small sample was often meshed, which could be too small to represent accurately the porous medium. Here, the use of a sample corresponding to the exact size used in the experiments permits the acquisition of accurate results. The shear stress resulting from flow through the bioreactor was obtained. The scaffold geometries were shown to influence the shear stress values, and therefore the cell formation. The study provided an insight into the mechanical loading that cells seeded onto the surface of a scaffold might sense. The methodology permitted the determination of WSS on each location of the scaffold, which can be used to correlate the WSS with the cell behavior in a scaffold. The use of DPLS allows for testing the geometry of a scaffold before using it in an in vitro experiment, which can reduce the costs of a study considerably.

In Chapter 5, a Monte Carlo ray tracing analysis on pore level was carried out based on a 3D geometry data set measured by computer tomography. The extinction coefficient $\beta$ and scattering phase function $F$ of a ceria RPC were successfully determined by the approach introduced in 2.13. These effective radiation transport properties will be the input parameters of a continuum model for a porous ceria absorber designed for the two-step production of syngas. The collision-based MC method determined the extinction path length and scattering angle of each traced ray. The evaluation of the probabilistic cord length distribution function led to an extinction coefficient of $278.74 \text{ m}^{-1}$. This value exhibited good agreement with the performed experimental transmission measurements on a spectroscopy system. The directional extinction coefficients in the three Cartesian axes were computed by a numerical experiment and comparable values were obtained; thus, the isotropy assumption was validated. The scattering phase function was calculated based on the probability distribution of the cosines of the scattering angles. Specular and diffuse reflection were distinguished; the former showed isotropic scattering behavior, while the latter was characterized by enhanced backward scattering. Both cases agreed quantitatively with the analytical solutions for scattering of large specular or diffuse spheres, respectively.

### 6.2 Outlook

The presented methodology showed to accurately characterize the morphological and mass transport properties of snow samples. However, since snow is in constant metamorphosis, its properties will change with time in the field. The new properties will in turn have an impact on the metamorphism itself.
Particularly, metamorphism and permeability have a mutual effect on each other [13]. A monitoring of this change would be possible by µCT. A following study on snow metamorphism under advective conditions has been initiated. The plan is to develop an experimental system where metamorphism under airflow can be quantified. In-situ time-lapse experimental runs will be first conducted in µCT on quasi-isothermal snow, and then extended on snow under a temperature gradient. A new sample holder is currently being designed for these experiments, which will permit the constant application of air flow and/or a temperature gradient on the sample and its regular scan by µCT. This would allow for the determination of the time-lapse evolution of the heat and mass transport properties of a snow sample. Vapor mass flux and recrystallization rate can be determined using an adapted version of particle image velocimetry based on time-lapse images. The dependence of the recrystallisation rate with the permeability of the snow would be examined. A functional understanding of snow metamorphism combined with airflow would give more solid understanding of the snow structure observed in polar and alpine regions.

In the field of bone tissue engineering, the presented study allowed for the characterization of a scaffold scanned by µCT before being seeded and subjected to a flow in a perfusion bioreactor. However, once in the bioreactor, the cells will fill up the space within the pores and, over time, they would surround themselves with ECM. Therefore, the properties of the scaffold will slowly change; its porosity will be reduced, as well as the pore size, which will have a direct impact on the wall shear stress. To keep the production of cells optimal, one has to adapt the inlet flow in order to influence shear stress distribution. To provide such a feedback, two options are possible: i) The scaffold can be regularly scanned by µCT to follow the evolution of tissue formation. Performing a study on each new scan would allow to follow the evolution of the scaffold properties and to adapt the inlet flow accordingly. However, once in liquid, the scaffold does not show a high contrast with its surrounding, which makes its characterization by µCT difficult. Taking the scaffold out of the liquid and drying it before each tomography would interrupt the biological process and therefore result in the disrupting of the experiment. Therefore, to be able to conduct such a study, the scanning in liquid should be improved to obtain a better contrast. ii) A second approach would be to mimic the bone tissue formation on the scaffold by image processing. Morphological operations could be applied, such as a dilation of the scaffold walls with a structuring element. This would result in a regular material increase in each pore of the scaffold. It would not correspond very closely to the experimental observations of cell formation, which does not form regularly, but would provide a first insight into the change of wall shear stress with a diminution of porosity and pore size. Other techniques of image pro-
cessing could be developed to account more closely for the tissue formation. For example, producing new material only on the fine edges would give a closer insight. Adding bone tissue as a function of the calculated shear stress would be a promising solution. A similar approach has already been used and could be adapted for the present methodology [163, 164]. The development of one of these techniques would allow the automation of in vitro bone tissue formation, and would give a better control over the geometry of the tissue formed, to correspond to the ideal graft needed to continue its formation in vivo.

Moreover, the presented methodology allows for the optimization of the scaffold geometry. Tests can be run with different scanned structures; morphological operations can be performed to determine the optimal porosity and pore size for an efficient bone formation. By controlling the scaffold microstructure in the manufacturing process, it could be possible to generate ranges of WSS that promote a certain type of tissue formation [89, 113, 131, 159].

Scanning the scaffolds in liquid would also improve the representation of their microstructure. Here the sharp features present in the scaffold due to the drying process were smoothed with a Gaussian filter; however, a direct scan in liquid would account more closely for the swelling of the scaffold in a wet state. Moreover, it would allow for a direct comparison between the simulated shear stress and the observed bone formation.

The ceria RPC presented in Chapter 5 has been already successfully used for CO$_2$ splitting via thermochemical redox reactions [56]. The RPC offers the advantages of a volumetric radiative absorption, rapid reaction rates and high mass loading of reactive material [56]. However, the fuel production step remains slow with the RPC, which is attributed to the low SSA of the structure [108]. To improve the reaction rate, a new RPC has been recently developed with a higher SSA, without losing the advantages of a RPC structure. The large pores are kept to allow for entering radiation and micropores of 5 to 10 µm are added into the existing struts of the former RPC. For this purpose, a modified slurry is used to produce the struts, containing a certain volume of spherical carbon particles used as fugitive pore formers [108]. The micropores are connected only for a volume of pore formers higher than 30%, which is necessary to allow mass flow through the struts, and therefore a higher reaction rate. Cross sections of a strut of RPC with 20% pore formers, and a strut of RPC with 50% pore formers obtained by µCT are shown in Figure 6.1. The heat and mass transfer properties of the microporous struts will be determined to develop a multi-scale volume averaging model, which can be visualized in Figure 6.2.

In the case of microporosity, the presented methodology to determine mass
Figure 6.1: Cross section of a strut of RPC obtained by \( \mu \)CT with 20\% (left) and 50\% (right) pore formers. The edge length is 0.832 mm. The pores on the left are not interconnected, while the pores on the right show a good interconnection, allowing for mass flow through the struts.

Figure 6.2: Visualisation of the 3 scales volume averaging of a microporous ceria RPC used in a solar thermochemical reactor.
transport might show some limitations. With a pore size between 5 and 10 µm, the Knudsen number would become too high to use the standard continuum formulation of fluid dynamics, and would rather be in a slip flow regime [44]. The methodology should therefore be adapted to take this case into account.

DPLS can be further applied to other materials. A packed bed of micro porous particles of manganese oxide is considered for its application in thermochemical storage via reversible redox reactions. The knowledge of the effective diffusivity and thermal conductivity within a bed granule is required to determine its ideal size. Multi-scale analysis can be performed to determine in turn the properties of the packed bed itself. More generally, the methodology presented allows for the optimization of any porous structure or packed bed of materials used in thermochemical cycles, such as zinc oxide, iron oxide or cerium oxide.

Other materials show an application in a wide range of fields. Amongst them are metallic foams, which offer a good thermal and acoustic insulation [157], filter beds of granular materials used for water treatment [133] and hollow bricks used for building structures [197]. Other applications to geophysics [23, 52], groundwater hydrology [21, 79] and soils science are proposed. The determination of flow and heat transfer in biological tissues are of interest [91].

The methodology can be further developed to characterize the anisotropy of morphological parameters. The determination of pore and grain size should be improved to account more precisely for irregular shapes. The Monte Carlo model for radiative properties could be adapted for materials of which reflectance changes with the incoming angle, and for materials presenting a reflectance type partly specular and partly diffuse. The mass transfer model could be developed for higher Knudsen number regimes: the slip regime (0.001 < Kn < 0.1), the transition regime (0.1 < Kn < 10) and the molecular regime (Kn > 10) [44]. In the case of anisotropic porous media, numerical simulations should be performed by applying a pressure gradient in all directions with respect to the microstructure in order to obtain the complete tensorial form of the extended Darcy’s law coefficients (Equation (2.17)). The transitional Re between second and third order Darcy’s law (Equations (2.16) and (2.15)) could be determined more precisely.

The methodology presented in this thesis showed to be a promising approach for the determination of morphological and heat/mass transport properties of various types of porous media. The proposed improvements would make it a method of choice for the characterization and optimization of com-
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[161] Scanco Medical AG, Brüttisellen, Switzerland. µCT40.


Curriculum Vitae

Name: Emilie Léonie Zermatten

Nationality: Swiss and French

Citizen of: St-Martin (VS)

Date of birth: July 28, 1985

2010-2013: Doctoral studies at the Professorship of Renewable Energy Carriers, ETH Zurich; supervision: Prof. Dr. Aldo Steinfeld


2004-2007: Bachelor studies in Physics at EPFL

2006-2007: Exchange year at the Indian Institute of Technology, Delhi (IITD), New Delhi (India)

1999-2004: Maturité cantonale at Lycée-Collège de la Planta, Sion (Switzerland)
List of publications

Journal Papers


Conference Proceedings


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