



DOCTORAL THESIS

A multiscale material description for wood below the fiber saturation point with particular emphasis on wood-water interactions

submitted in satisfaction of the requirements for the degree of Doctor of Science in Civil Engineering of the Vienna University of Technology, Faculty of Civil Engineering

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Ein Mehrskalenmodell für Holz unter dem Fasersättigungspunkt unter besonderer Berücksichtigung der Wechselwirkungen zwischen Holz und Wasser

ausgeführt zum Zwecke der Erlangung des akademischen Grades eines Doktors der technischen Wissenschaften eingereicht an der Technischen Universität Wien, Fakultät für Bauingenieurwesen

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Everything should be made as simple as possible – but no simpler. $Albert\ Einstein$

Man soll die Dinge so einfach machen wie möglich – aber nicht einfacher. Albert Einstein

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Kurzfassung

Sowohl in der Holzforschung als auch im Ingenieurholzbau ist eine korrekte mathematische Beschreibung des Materials von größter Bedeutung. Im Falle von Holz ist das schwierig, handelt es sich doch um ein Material mit ausgeprägter Orthotropie und zeitund feuchteabhängigem Verhalten. Einen weiteren Einfluss auf die Materialeigenschaften haben unter anderem Holzart, Wachstumsbedingungen, Dichte sowie Temperatur. Dies hat eine breite Streuung sämtlicher Materialeigenschaften zur Folge, sogar innerhalb ein und desselben Baumes. Aufgrund dieser Tatsachen scheint die Formulierung eines universell anwendbaren Materialmodells beinahe unmöglich.

Das Ziel der vorliegenden Arbeit ist es, die dem beobachteten (makroskopischen) Materialverhalten zugrundeliegenden Prozesse zu verstehen und darauf aufbauend ein physikalisch korrektes Materialmodell zu formulieren. Ausgangspunkt dafür ist die dem Material eigene Mikrostruktur. Holz weist eine optimierte und streng hierarchisch gegliederte Struktur auf, beginnend bei den mit freiem Auge sichtbaren Jahresringen über die Zellstruktur bis hin zu den Holzpolymeren Zellulose, Hemizellulose und Lignin auf der Molekülebene. Auf dieser kleinen Längenskala lassen sich die Ursachen für das zeitabhängige Verhalten von Holz sowie dessen Interaktion mit Wasser identifizieren. Aufbauend auf diesen Grundlagen wird anschließend eine thermodynamisch korrekte, makroskopische Beschreibung für Holz formuliert. Sie besteht aus Massenerhaltungsgleichungen für die beiden Wasserphasen, einem Energieerhaltungssatz sowie den mechanischen Gleichgewichtsbedingungen. Zusammen mit den konstitutiven Gleichungen steht hiermit eine allgemein gültige Materialbeschreibung zur Verfügung, mit klar definierten Anwendungsgrenzen bei verschiedenen Sonderfällen.

Mithilfe der Kontinuumsmikromechanik werden die benötigten Materialeigenschaften bestimmt. Bei Verwendung dieser Methode wird die Mikrostruktur von Holz mathematisch nachgebildet, was die Abschätzung von Materialeigenschaften für ein bestimmtes Stück Holz ermöglicht. Auf Grundlage dieses Konzepts werden Modelle für die Wärmeleitfähigkeit, den stationären Diffusionskoeffizient von Wasser sowie das zeitabhängige mechanische Verhalten von Holz präsentiert. Anhand von Vergleichen zwischen experimentell bestimmten Materialparametern und entsprechenden Modellvorhersagen wurden die Modelle erfolgreich validiert.

Ein weiterer wichtiger Prozess ist die Aufnahme und Abgabe von Wasser durch die Zellwand (Sorption). Um diesen zeitabhängigen Prozess korrekt beschreiben zu können, wird ein analytisches Sub-Modell einer Holzzelle hergeleitet. Weiters gezeigt wird eine physikalisch plausible Erklärung für die Sorptionshysterese. Für diese Theorie werden Poromechanik, zeitabhängiges Materialverhalten sowie Thermodynamik kombiniert.

Die abschließenden Kapitel befassen sich mit instationären Transportprozessen in Holz unter dem Fasersättigungspunkt. Nach Ermittlung der benötigten Materialparameter wird eine numerische Lösung des resultierenden Gleichungssystems mittels der Methode der finiten Elemente präsentiert. Auch dieses Modell wurde anhand zweier experimenteller Versuchsreihen (improved cup method, Kernspinresonanzspektroskopie) validiert. Sämtliche experimentellen Ergebnisse konnten mit dem Modell vorhergesagt werden, erneut ohne Verwendung rückgerechneter Faktoren oder sonstiger unphysikalischer Parameter. Es steht nun erstmalig ein Modell zur Verfügung, das auf einer physikalisch korrekten Materialbeschreibung basiert und somit zuverlässige Vorhersagen ermöglicht.

Abstract

In wood science as well as in timber engineering, a suitable material description is of utmost significance. However, wood is not a "simple" material, it rather exhibits a timedependent, orthotropic material behavior, which in addition depends amongst others on wood species, growing conditions, density, moisture content, and temperature. This leads to strong variations in material properties even within one tree. Overall, the strive for a universal material model seems almost impossible.

This thesis aims at a deeper understanding of the processes and the physical basics that influence the observed (macroscopic) material behavior and, finally, at the derivation of a physically correct mathematical material description. For this purpose, the material's microstructure is investigated first. Wood is a well-organized and hierarchically structured material – from the annual rings on the macroscale down to the basic wood polymers cellulose, hemicellulose, and lignin on the molecular scale. On this small length scale, the origin for the time-dependent material behavior and the interaction with water can be identified in a physically correct manner. Based on these findings, a macroscopic continuum description for wood is given afterwards. It comprises balance laws for the different water phases, energy, momentum and momentum of momentum. Information about the material comes in through constitutive equations and according material properties. This comprehensive and generally applicable set of equations is then adapted for relevant special cases (e.g. steady state moisture transport) with clearly defined limits of applicability.

The material properties of wood are derived in the framework of continuum micromechanics. This method allows to give estimates for a particular piece of clear wood (wood without growth irregularities like knots) by reproducing the hierarchical structure of wood in a mathematical way. Within this concept, models for thermal conduction, steady state moisture diffusion, and the viscoelastic mechanical behavior of wood are formulated and successfully validated by comparing model predictions to according experimental results at the clear wood level.

An important process in wood-water interrelations is sorption, describing the uptake and release of moisture by the wood cell walls. In order to describe this time-dependent process, an analytical sub-model for the structure of a wood cell is derived. In addition, a suitable theory for the description of sorption hysteresis is given by combining poromechanics (extended by time-dependent mechanical behavior) and thermodynamics.

The last chapters of this thesis deal with the special case of transient transport processes at structural level in wood below the fiber saturation point. After clarifying the thereon needed material properties, a numerical solution of the mathematical problem in the framework of the finite element method is derived. For validation purposes, two series of experiments were conducted using an improved cup method and proton magnetic resonance imaging (NMR). All experimental results are suitably predicted by the model without any back-calculated or unphysical parameters, underlining again the quality of the model. Thus, unlike previous modeling attempts, the model accomplishes physically correct and reliable predictions for such processes.

Comment on the structure of this thesis

This thesis is based on eight publications in peer-reviewed international journals. Instead of assembling these publications to a cumulative dissertation, a coherent monograph was written in addition. Thus, the advantages of both types of theses could be combined.

In the monograph, the eight own journal articles are not explicitly cited. However, their published versions are appended at the end of this thesis for documentation. The author's contributions to these articles are as follows:

- **Publication 1:** Composites Science and Technology 71 (2011) 134–144 Developed the multiscale homogenization model. Performed the validation of the model. Did most of the preparation of the manuscript.
- **Publication 2:** Composites Science and Technology 71 (2011) 145–151 Developed the multiscale homogenization model. Performed the validation of the model. Did most of the preparation of the manuscript.
- **Publication 3:** Wood Material Science and Engineering 5 (2010) 97–103 Developed the multiscale homogenization model. Performed the parameter studies. Did most of the preparation of the manuscript.
- **Publication 4:** *Holzforschung* 65 (2011) 337–342 Clarified the physical background. Formulated the according macroscopic set of equations. Had the idea for the submodel for the description of sorption. Did most of the preparation of the manuscript.
- Publication 5: Composites Science and Technology 71 (2011) 1727–1738 Formulated the problem. Developed and implemented the Finite Element model. Planned and evaluated the results of the SilviScan measurements together with K. Hofstetter. Measured the sorption isotherm. Performed the validation of the model. Did most of the preparation of the manuscript.
- **Publication 6:** Transport in Porous Media revision submitted for publication Performed the experiments except for the determination of boundary conditions. Did most of the preparation of the manuscript.
- **Publication 7:** International Journal of Thermal Sciences 50 (2011) 1861–1866 Developed and implemented the Finite Element model. Performed the validation of the model. Did most of the preparation of the manuscript.
- **Publication 8:** Computational Materials Science submitted for publication Completed the development of the multiscale homogenization model. Performed the validation of the model. Did most of the preparation of the manuscript.

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Chapter **1**

Introduction

1.1 Motivation

Wood is currently facing a revival in the construction sector all over the world and is increasingly used, both for common building and for special engineering purposes. To meet the resulting high demands on wood in design and dimensioning, accurate knowledge of the material behavior is necessary. However, due to its natural origin the material properties of wood exhibit a broad variability, not only between different wood species, but also within one tree. In addition, the actual behavior of wood is strongly related to its moisture content. All these facts complicate the derivation of a suitable material description. Existing material models are mostly restricted to subproblems like the mechanical behavior, swelling/shrinkage, heat transport or moisture transport. The problems of these isolated views are their inexplicit limits of applicability – in some cases they are efficient, in other cases they fail or lead to strange results, which are then labeled as "phenomena" or "special behavior". At the moment this lack of knowledge is tackled by material modification factors (for the influence of the climatic conditions and the long-term material behavior) and high safety coefficients in timber engineering. This results in partly inefficient timber structures, which still cannot ensure the desired reliability of the constructions.

This thesis aims at a deeper understanding of the material wood and at a physically correct description of appearing processes. This will be the scientific basis for a more reliable, efficient, and intelligent use of this fascinating material.

1.2 Previous work

Comprehensive material descriptions for wood are rare in literature. In the 1950s, Barkas [5] was one of the first to discuss the thermodynamical background of sorption, swelling, and the mechanical behavior of wood. A macroscopic continuum description of wood

was given in 1971 by Lesse and Christensen [60] in the framework of non-linear thermodynamics. However, owing to the stage of development in computer science at that time, numerical solutions of coupled problems were almost unaccessible and, in addition, some of the required material parameters were not known. Therefore no relevant publications in this field can be found from the following years, rather the focus was on particular topics like moisture transport or the sophisticated mechanical behavior of wood.

As for models that allow for a macroscopic mathematical description of moisture transport processes in wood, a lot of theoretical and experimental work was done. Below the fiber saturation point, moisture transport was accepted to be governed by a single diffusive process [55], which is usually described by Fick's law of diffusion. On this theoretical basis, experimental work was done in the 1960s to define the according diffusion coefficients [11, 10] based on a macroscopic gradient in moisture content. Under steadystate conditions this approach led to suitable and reproducible results – in contrast to transient conditions, where some unphysical phenomena like thickness-dependent diffusion coefficients were observed. These findings motivated theoretical research (see e.g. [97, 72, 96]), mostly focusing on the macroscopic formulation of non-isothermal moisture transport in wood. In parallel, the progress in computer technology allowed for the first time numerical studies of non-linear and coupled moisture transport processes [106, 78]. In these models, three differential equations describe conservation of liquid, energy, and air inside wood. They allow for numerical studies of drying processes in wood, including high temperature conditions and sample-specific material properties and geometries. However, no validation (i.e. a comparison with an independent set of experimental results) of these models is given in literature.

At the same time another approach to the description of transient moisture transport was developed [57, 27]. Its main idea is to describe the microscale transport processes on their inherent length scale, to formulate based thereon two separate Fickian diffusion processes for bound water and water vapor, and to couple these phases by a sorption rate term. The advantage of this approach is that it more suitably describes the physics of moisture transport in wood since it abandons the joint treatment of water vapor and bound water which is impossible because of disequilibrium of the average concentrations of these two phases under transient conditions. This allows for a more realistic description of experimentally derived results. However, the sorption term is described phenomenologically. It has to be fitted to experimental results, which limits the applicability of this approach to non-tested conditions.

The mentioned material descriptions all involve material properties. For wood these show a high variability, originating from differences between wood tissues at the macroscale, microscale, and nanoscale. This fact motivated quite many research efforts to establish links between the macroscale and physical quantities at lower scales. As for transport properties, the most common approach is to define a single tracheid as representative "unit-cell" and to formulate relations between the transport properties and apparent densities as well as moisture contents of wood [95, 104, 35, 77] on this basis. However, many of the required material data, especially the material properties of the cell wall, are not known from experiments. The need to guess or back-calculate material parameters [95, 104] limits the applicability of such models to tested conditions.

The use of wood as a construction material of course also requires detailed knowledge about its mechanical properties. Since this is directly related to an economic use of

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the material, a multitude of studies was made in this regard, both experimentally and theoretically. The idea of relating the macroscopic behavior to smaller length scales of the material was also successfully applied to mechanical properties, a comprehensive review of according models for wood is given by Hofstetter and Gamstedt (2009) [43].

1.3 Scope and Structure

In wood science, a multitude of different material models is used. The aim of this thesis is to derive a physically correct and therefore generally applicable material description for wood below the fiber saturation point with particular emphasis on the interaction of wood and water. The material behavior of wood is strongly influenced by its microstructure, this information is incorporated via multiscale homogenization approaches, that link the macroscopic behavior of wood to its basic constituents and processes on the molecular scale. Finally, the performance of the model is checked by comparing model predictions to independent experimental results. The gained excellent prediction quality justifies the extensive formulation of the approach.

From a macroscopic point of view wood exhibits a complex behavior, that complicates a suitable material description or even makes it impossible. However, the origin of this behavior is the structure and composition on the material's smaller length scales. In addition, the interaction between wood and water can be explained – at least qualitatively – on the microscale. Therefore the thesis starts with an comprehensive investigation of this physical background of the material behavior of wood in Chapter 2.

Based on this background, a macroscopic continuum description is given in Chapter 3. It comprises balance equations for energy, momentum, momentum of momentum, and the masses of the water phases in wood. In addition, the according constitutive relations are introduced which define the material. This comprehensive set of coupled equations is then specified for some special cases, which are important e.g. for validation purposes.

Although the description of wood is formulated on the macroscale, the information about the material on the smaller length scales has to be included. This is done via the material properties used in the constitutive relations. In the framework of continuum micromechanics it is possible to upscale the material behavior from small scales to the macroscale. Starting from the molecular scale, where a few basic constituents of wood can be defined, the hierarchical structure of wood. In this line models for several material properties are developed and presented in this thesis: a multiscale homogenization model for thermal conductivity in Chapter 4, a model for steady state moisture diffusivity in Chapter 5, and – predicated on an existing model for elastic properties – a model for viscoelastic material behavior in Chapter 6. Based on basic information – wood species, density, temperature, and moisture content – these models allow for suitable estimations for specific wood samples. This is verified by comparison with experimentally derived results.

In Chapter 7, a mathematical description for sorption is derived. Sorption is the exchange process between water vapor in air and bound water in the wood cell walls. Again a multiscale approach enables a suitable macroscopic description of this process. The driving force of sorption is the strive to reach equilibrium between the two water phases. Such conditions can be described via sorption isotherms, relating a given relative humidity to an according equilibrium moisture content. For wood, these sorption isotherms possess a distinct hysteresis, i.e. the equilibrium moisture content is not unique for a specific relative humidity but depends on sorption history. To account for this effect, an empirical and a possible theoretical description are given, the latter by accounting for the time-dependent deformations of the wood cell wall.

The last Chapters deal with the special case of transient moisture transport in wood. After definition of several additional material parameters in Chapter 8, a numerical solution procedure for the according mathematical problem in the framework of the finite element method is derived in Chapter 9, including the implementation in the commercial finite element code ABAQUS. Together with the sample-specific properties estimated using the multiscale homogenization models this enables predictions of transient moisture transport processes in wood. Verification of this approach is again based on comparison with experimental results. This is done in Chapters 10 and 11 for results gained with an improved cup method and nuclear magnetic resonance imaging, respectively. The latter allows for non-destructive investigation of moisture distributions inside a material. In both cases a good prediction quality will be shown, proving the suitability of the whole modeling approach.

Finally, this thesis is concluded in Chapter 12.

1.4 Nomenclature

Symbols

a	ellipsoidal radius
A	area
b	external energy source
b	Biot tensor
с	concentration
\hat{c}	microscopic concentration
\dot{c}	sorption rate
c_V	specific heat capacity at constant volume
\mathbb{C}	stiffness tensor
D	diffusion tensor
\mathbb{D}	compliance tensor
e	specific internal energy
E	internal energy
E	modulus of elasticity
\mathbf{E}	macroscopic strain tensor
$\mathbf{E}^{ ext{el}}$	macroscopic elastic strain tensor
$\mathbf{E}^{ ext{pl}}$	macroscopic plastic strain tensor
EMC	equilibrium moisture content
$arepsilon_r$	strain within phase r
f	volume fraction
f	heat flux
g	body force vector
G	shear modulus

4

Symbols cont'd

h	specific enthalpy
Ι	second order unity tensor
I	fourth order unity tensor
J	creep compliance
J	mass flux
k	film boundary coefficient
K	thermal conductivity tensor
κ	mass supply rate
l	length
λ	thermal conductivity
m	mass
M	molar mass
MC	moisture content
μ	chemical potential
n	normal vector
Ν	interpolation function
N	number of molecules per volume
ν	Poisson's ratio
p	pressure
Р	second order Hill tensor
\mathbb{P}	fourth order Hill tensor
ϕ	surface flux
ϕ	cell wall porosity
φ	relative humidity
r	radius
R	universal gas constant
\mathbb{R}	relaxation tensor
ρ	mass density
s	specific entropy
s	complex variable in the Laplace-Carson domain
s	dimensionless sorption parameter
S_{-}	entropy
S	surface
$oldsymbol{\sigma}_r$	stress within phase r
Σ	macroscopic stress tensor
t	time
t	cell wall thickness
T	temperature
θ	microfibril angle
Θ	Heaviside function
u	displacement vector
V	volume
x	coordinate vector
ξ	reduction factor for vapor diffusion in wood

Subscripts / Superscripts

-	
0	initial
a	adsorption
a	ambient
air	air
amocel	amorphous cellulose
ann	annual rings
ash	ash
atm	atmospheric
b	bound water
cel	cellulose
circcyl	right circular cylindrical
crvcel	crystalline cellulose
cwm	cell wall material
d	desorption
drv	dry (without any water)
early	earlywood
ell	ellipsoidal
ellcyl	elliptic cylindrical
exp	experimental
ext	extractives
H_2O	water
hemcel	hemicellulose
hom	homogenized
iso	isotropic
late	latewood
lig	lignin
long	longitudinal
lum	lumen
L	macroscopic longitudinal material direction
MT	mori Tanaka scheme
θ	standard conditions
poly	polymer network
por	porosity
ray	ray cell
ref	reference
rot	rotated
R	macroscopic radial material direction
s	solid wood material
sat	saturated
sph	spherical
SC	self-consistent scheme
trans	transversal
Т	macroscopic tangential material direction
v	water vapor
ves	vessel
wet	wet (including water)
wood	wood (macroscale)

Subscripts / Superscripts cont'd

	parallel
\perp	perpendicular
*	Laplace-Carson domain

Accents used in the multiscale homogenization models

	relating to an representative volume element (RVE) of polymer network
	relating to an representative volume element (RVE) of cellulose
	relating to an representative volume element (RVE) of cell wall material
	relating to an representative volume element (RVE) of earlywood
Ě	relating to an representative volume element (RVE) of latewood
·	relating to an representative volume element (RVE) of ray cells
Ē	relating to an representative volume element (RVE) of earlywood with vessels
	relating to an representative volume element (RVE) of annual rings
	relating to an representative volume element (RVE) of clear wood

Chapter 2

Physical Background

Wood exhibits strongly anisotropic, time-dependent material behavior. It shows different failure mechanisms depending on the load type and loading direction, for example brittle fracture under tension load in grain direction and plastic deformation (within certain limits) under a pressure load across the grain. In addition it shrinks and swells upon changes in moisture content, its material properties are dependent on moisture content and temperature, and it may be destroyed by fungi, insects, and fire. Finally, each piece of wood exhibits individual material behavior. Overall, a correct purely macroscopic description of the material wood is very complicated and sometimes seems to be almost impossible.

The macroscopic behavior of wood is influenced by morphology, chemical composition and processes on lower length scales. By observing these scales, many macroscopically observed phenomena can be explained on a scientific basis. Further, knowledge about the physical background enables the derivation of suitable mathematical descriptions, which then may help to understand and, ideally, to predict the material behavior.

In this chapter the morphology and processes inside wood are recapitulated, particular attention is paid to water and its interaction with wood.

2.1 Composition and structure of wood

Wood is a fascinating biological material with a highly optimized and specialized structure on several length scales – from the molecular scale up to the structural scale of a tree. This thesis is restricted to so-called clear wood, which is wood without structural growth irregularities like knots or spiral growth [26, 37]. Following pertinent work in the field [56, 73, 25, 110], one may distinguish six levels of organization in clear wood.

The stem cross-section of wood is built up by the sequence of earlywood and latewood, formed in concentric rings [see Fig. 2.1(a)]. These growth or annual rings with origin in the center of the stem are a consequence of the growing process during each season. They

result in the three macroscopic principal material directions of wood – the longitudinal (L), radial (R), and tangential (T) direction. The longitudinal direction coincides with the longitudinal axis of the stem (except for spiral grain), while the radial direction points normal to the annual rings. Hence, the tangential material direction is defined by the local tangent to the annual rings. The typical length scale of the annual rings is 2 to 4 mm. At a similar length scale, wood rays form can be observed, they form pathways throughout the whole stem in the radial direction [see Fig. 2.1(b)].

On a length scale of several tens of micrometers, several types of wood cells are observed. Softwood species consist to the main part of tracheids, which are hollow tubes aligned in the stem direction with characteristic cell diameters of 20 to 50 μ m, lengths of 2 to 10 mm, and wall thicknesses of 2 to 20 μ m [cf. Fig. 2.1(c)]. In earlywood, the tracheids have thin cell walls with larger lumens and a polygonal or rectangular cross-section. By contrast, the latewood cells have thick cell walls and smaller pores. Tracheids are formed by division of the same initial cell in the cambium. Thus the cells are elongated in the radial direction, while in the tangential direction they are randomly arranged.

Hardwood species are younger in biological evolution compared to softwoods and exhibit a more diversified microstructure, including different specialized cell types. Tracheids, fibers, and parenchyma cells constitute the longitudinally oriented tissue, all of them showing similar dimensions. Moreover, hardwood species contain vessels of large diameters up to 500 μ m, which form an interconnected pipe-like structure (cf. Fig. 2.1(d)).

Wood rays are built up by single cells too, showing approximately circular cross-sections (Fig. 2.1(b)), diameters of 20 to $50 \,\mu\text{m}$, lengths of 50 to $500 \,\mu\text{m}$, and wall thicknesses of 2 to $20 \,\mu\text{m}$. In the living tree one function of all wood cells – both in softwood and hardwood species – is the transport of water and nutrients. For this purpose, neighboring cells are interconnected by pits.

The cell wall is characterized by sequentially arranged layers. From the lumen towards the outer surface of the cell there is the tertiary layer (T), the secondary layer 2 (S2), which represents about 80-90% by volume of the entire cell wall, the secondary layer 1 (S1), and the primary cell wall (P). Finally the compound middle lamella (CML) connects the single wood cells. All layers differ in thickness (see Fig. 2.1(e)) and in the fractions and arrangements of their constituents as detailed next.

In the cell wall layers, cellulosic fibers are embedded in a non-cellulosic matrix. These fibers have diameters of about 50 to 200 nm [73] and are divided into smaller microfibrils (see Fig. 2.1(f)). The orientation of these microfibrils varies from layer to layer. In the S2 layer, the inclination angle of the fibers to the cell axis (microfibril angle θ) typically ranges between 0° and 30° in normal wood. The cellulose microfibrils itself are composed of cellulose chains (see Fig. 2.1(h)). Only the inner core of a fibril is crystalline, while the surface region is more or less amorphous [76].

Finally, the embedding matrix is built up by non-cellulosic polysaccharides (commonly denoted as hemicelluloses), lignin, extractives, and inorganic compounds. Lignin and hemicelluloses constitute the major part. Extractives and inorganic compounds make up only 2 to 4% in volume. The typical length scale of the mixture of the constituents is about 8 to 20 nm [38]. An example of the molecular structure of lignin is shown in Fig. 2.1(g). In addition, water molecules intrude into the matrix and are absorbed physically at sorption sites (hydroxyl groups) that are mainly located on the polysaccharides.



Figure 2.1: Hierarchical organization of wood (extended version of Fig. 2 in [44]): (a) cross-section of a $\log^{(1)}$; (b) longitudinal section through a hardwood (*Betula alba*), showing the ray cells, Transmission electron micrograph (TEM)⁽⁴⁾; (c) transverse section through a softwood (*Picea abies*), Transmission electron micrograph (TEM)⁽⁴⁾; (d) transverse section through a hardwood (*Fraxinus excelsior*), Transmission electron micrograph (TEM)⁽⁴⁾; (d) transverse section through a hardwood (*Fraxinus excelsior*), Transmission electron micrograph (TEM)⁽⁴⁾; (e) section through the cell wall, showing the cell wall layers⁽²⁾; (f) fibrillar structure of the S2 (and S1) wall⁽³⁾; (g) chemical structure of lignin⁽⁵⁾; (h) model of the crystal structure of a cellulose chain⁽⁵⁾; ⁽¹⁾...adapted from Wood Handbook [107]; ⁽²⁾...adapted from Fengel and Wegener [25]; ⁽³⁾...adapted from Hafren et al. [38]; ⁽⁴⁾...adapted from Schoch et al. [93]; ⁽⁵⁾...adapted from Wikipedia

This bound water has a huge influence on almost all wood properties, therefore it will be discussed in detail in the following section.

2.2 Water in wood

Water can be found in wood not as bulk phase, it rather exists in three states in parallel. They exhibit different properties and affect the material wood in different ways.

2.2.1 Liquid water

The first state is liquid water located in the cell lumens. It solely exists in the living tree or in wood being in contact with liquid water. When wood is exposed to air, the liquid water evaporates (except for capillary condensation that occurs in presence of a relative humidity in air above 98 %, see [22]). The influence of liquid water on mechanical properties is negligibly small [55], while it is a precondition for biological degradation due to fungal growth. Therefore, wood is dried before it is used for constructional purposes, and it has to be protected from permanent contact to liquid water (ideally by means of constructional wood protection). The transport of water is mainly governed by a flow process driven by pressure gradients. This flow is important for the tree because thus minerals are transported inside the stem; it is enabled by the open pits interconnecting the cell lumens. When the moisture content decreases, the pits get aspirated to prevent the tree from loosing liquid water; in consequence water transport is decelerated dramatically.

2.2.2 Water vapor

During wood drying, the liquid water in the cell lumens is replaced by air, that comprises water vapor, i.e. the second state of water in wood. As long as liquid water and water vapor are present at the same time, the relative humidity of air is approximately 100%. However, on the surface of wood the relative humidity inside the lumens and in the ambience is equal, therefore all liquid water inside wood evaporates when the surrounding relative humidity is below 100%. The main transport process of water vapor inside wood is diffusion, driven by gradients in chemical potential which is mainly a function of vapor concentration in air and temperature. The flow of air is effectively retarded by the closed pits that block the throughgoing pathways in wood.

2.2.3 Bound water

As long as liquid water is present, the cell walls are saturated with bound water – the third occurrence of water in wood. It consists of water molecules that are physically bound to the sorption sites as mentioned in the previous section. The point, where no liquid water is present but the cell walls are still saturated is called the fiber saturation point (FSP), such a condition is present at about 100 % relative humidity and a moisture

content (usually denoted as MC or u) of about $30 \%^1$. Subjected to lower relative humidities, also the cell walls start to dry – the bound water concentration inside the cell walls decreases. In contrast to the other two water phases (liquid water and water vapor), changes in bound water concentration strongly affect the material behavior of wood and lead to changes in volume of the cell walls. Due to the anisotropic morphology of wood these eigenstrains lead to eigenstresses inside the material, in addition they cause the shrinkage and swelling observed on the macroscale.

Bound water is transported by a diffusive process, the according diffusion coefficient strongly depends on bound water concentration. The driving force of this process is the chemical potential of bound water, which is a function of concentration, temperature, the chemical composition of the cell wall (which influences the number and interaction of the sorption sites) and pressure due to stresses inside the cell wall. Water may also change its state; for changes from bound water to water vapor and vice versa this is called sorption. Equilibrium conditions between these two phases imply equal chemical potentials. The equilibrium moisture content (EMC) for wood is therefore a function of relative humidity, temperature, chemical composition of the cell wall, mechanical state, and history. For practical reasons the equilibrium conditions are described by sorption isotherms, plotting EMC against relative humidity. These sorption isotherms are not unique for a specific relative humidity but show a pronounced hysteresis effect, indicating that the EMC is not solely a function of relative humidity and temperature. Additionally, due to different chemical composition each sample of wood exhibits its individual sorption behavior.

Overall, the interaction of wood with water is of greatest importance for a comprehensive understanding of the material. Therefore, the governing processes will be defined in the following sections to serve as physical background for the modeling work shown later on. In wood used for constructional purposes, conditions below the fiber saturation point are prevailing. Therefore this thesis is restricted to such conditions, where only two water phases are present: bound water in the cell walls and water vapor in the lumens.

2.3 Transport of water on the microscale

As mentioned in the previous chapter, both bound water and water vapor are transported by diffusion. The physical foundation of moisture transport in wood can be best studied on the microscale, where the phases bound water and water vapor can be clearly distinguished.

2.3.1 Static conditions

In Fig. 2.2, a cell wall cross-section and the water concentrations for equilibrium conditions are displayed schematically. The cell wall contains bound water with a concentration of c_b (calculated as mass of bound water divided by the volume of pure cell wall material), while the lumens contain water vapor with a concentration c_v (calculated as mass of water vapor divided by the volume of pure air). Since the gradients of the

¹The moisture content in wood is usually calculated by relating the mass of water in wood to the oven-dry mass of the same wood sample.

concentrations c_b and c_v have to be zero under static conditions, no moisture transport will take place within the phases. On the boundaries between lumens and cell wall the concentrations are in equilibrium (e.g. described by a sorption isotherm). When water changes from one phase to the other, the phase transition is accompanied by a change in entropy S of water:

• water vapor \rightarrow bound water "adsorption" $\Delta S_{\text{H}_2\text{O}} < 0$, • bound water \rightarrow water vapor "desorption" $\Delta S_{\text{H}_2\text{O}} > 0$.

To accomplish a phase transition, energy must be supplied or adsorbed by the surrounding. This leads to a increase in internal energy E in the surrounding during adsorption of water and to a decrease in internal energy for desorption. This change in internal energy is accompanied by changes in temperature T and volume V of the system $(dE = C_V dT + [T(\partial p/\partial T)_V - p] dV)$. In wood the first is predominant, therefore the phase change of water mainly causes changes in temperature (a temperature increase for adsorption, a temperature decrease for desorption). Under static conditions (Fig. 2.2), no moisture transport occurs and, thus, no phase transition and no changes in energy and temperature².



Figure 2.2: Moisture and heat transport at the microscale under static conditions.

2.3.2 Steady state conditions

In a steady state moisture transport process below the fiber saturation point, water is transported by diffusion. The cell wall and the air in the lumen exhibit specific diffusion coefficients, which depend on water concentration and temperature. *Steady state conditions* implicate constancy of concentration and temperature in each material point over time. Accordingly, on the boundary between cell wall and lumen the two phases are still in equilibrium (Fig. 2.3).

²From the standpoint of statistical mechanics water always changes its phase. Under static conditions the amounts of adsorbed and desorbed water are equal on average.



Figure 2.3: Moisture and heat transport at the microscale under steady state conditions.

The concentration gradient results in a diffusive moisture flux \mathbf{J} , which is equal in both phases to satisfy mass balance. The adsorption of water vapor to bound water on the left hand side of the cell wall in Fig. 2.3 is accompanied by energy release. On the right hand side of the same cell wall, desorption of bound water to water vapor is endothermic and, thus, results in absorption of energy. The amounts of water adsorbed and desorbed on opposite sides of one cell wall are equal in steady state processes. Therefore, also the amounts of energy released and absorbed are equal. They lead to a microscopic heat flux \mathbf{f} in the cell wall in the direction of the moisture flux \mathbf{J} . From a macroscopic point of view, there is no change in energy and temperature, i.e., $\partial E/\partial t = 0$, where E denotes the macroscopic internal energy and t the time.

For these two reasons – macroscopic isothermal equilibrium of bound water and water vapor (according to a sorption isotherm), no macroscopically relevant change in energy due to transport processes – steady state diffusion in wood can be described as single Fickian diffusion process on the macroscale. A possible additional thermal conduction process at the macroscale can be treated independently from the diffusion processes, because all thermal processes resulting from the moisture transport occur on a microscopic scale only and do not produce macroscopic relevant heat fluxes or temperature gradients.

2.3.3 Transient conditions

In transient processes, the state variables, namely moisture concentrations c_b and c_v and temperature T, change with time. To explain the physical background of transient transport processes, the special case of drying of small piece of wood with cutted lumens is considered (Fig. 2.4). Therein, the macroscopic moisture transport is mainly controlled by water vapor diffusion in the cut lumens in the longitudinal direction of wood. The macroscopic gradients of water vapor and bound water in the transverse direction of wood are approximately zero, leading to no macroscopic moisture flux in this direction. In addition to the macroscopic transverse moisture flux (which is equal to zero in this case), local concentration gradients develop in the transverse direction of the cell wall towards the lumens (Fig. 2.4). The macroscopic bound water concentration, c_b , is the mean value of the variable microscopic distribution of bound water concentration, \hat{c}_b . At each cell wall surface, the microscopic bound water concentration is in equilibrium with the water vapor concentration in the adjacent lumen. However, from a macroscopic point of view, there is an imbalance between macroscopic bound water concentration c_b and water vapor concentration c_v (Fig. 2.4). This imbalance prohibits treatment of the two water phases as one on a macroscopic level.



Figure 2.4: Moisture and heat transport at the microscale under transient conditions.

The special drying case in Fig. 2.4 involves desorption on both surfaces of the cell wall. Thus, energy is absorbed on both sides of the cell wall, resulting in an energy decrease also influential on the macroscale $(\partial E/\partial t < 0)$, which further leads to a macroscopic temperature decrease. The relevance of this thermal effect will be illustrated by a simple numerical example: theoretically, the removal of all bound water by desorption from a fiber-saturated piece of wood ($MC \approx 30\%$) with a density of $400 \,\mathrm{kg/m^3}$ requires energy of approximately 280 MJ/m³ (using thermodynamic quantities according to Skaar [98]). If the surroundings would not supply heat, this process would lead to a theoretical decrease in temperature of 410 K (considering a specific heat of wood of approximately $1.7 \,\mathrm{kJ/(kg\,K)}$ [112] and neglecting the mechanical work). In reality, such a significant decrease has never been measured and certainly does not occur. The reason for this is the dependence of the equilibrium moisture content in wood on temperature. This influence is displayed in Fig. 2.5 showing sorption isotherms for temperatures of 15 $^{\circ}$ C to 25 °C (calculated according to the Wood Handbook of the Forest Products Laboratory [107]). Usually, sorption isotherms are plotted for relative humidity on the abscissa; here, the water vapor concentration c_v is chosen instead to better illustrate the investigated example and the following considerations.

At point (1) in Fig. 2.5, the sorption isotherms indicate equilibrium of a water vapor concentration c_v of $17 \,\mathrm{g/m^3}$ and a moisture content MC of approximately 19% at a



Figure 2.5: Sorption isotherms for wood at temperatures from 15 °C to 25 °C, as a function of water vapor concentration.

temperature of 22 °C. Decreasing the water vapor concentration to 14 g/m^3 would result in an moisture content MC of approximately 13.5%, if T is kept constant (point 2) in Fig. 2.5). However, such a change in bound water content is accompanied by a considerable absorption of energy. As the sorption process on the microscale is faster than the heat transfer on the macroscale, this results in local decrease in temperature and, thus, in another equilibrium moisture content according to the prevailing sorption isotherm in Fig. 2.5. The corresponding point (3) is only slightly below the equilibrium moisture content at point (1). To reach lower moisture contents, heat has to be supplied to the wood sample to balance the absorbed energy during desorption. Such energy transfer is usually achieved by thermal conduction in the wood sample.

Based on these theoretical considerations, a correct macroscopic mathematical description of transient moisture transport in wood requires a separated treatment of the two water phases. In addition, an energy balance has to be one part of such a description.

2.4 Mechanical behavior of the cell walls

Besides the honeycomb-like cell structure of wood the mechanical behavior of the cell wall material has the widest influence on the macroscopic mechanical behavior of wood. Again an optimized structure can be observed in the cell walls. Together with the noncellulosic matrix material the cellulose microfibrils constitute a fiber-reinforced composite. The highly oriented microfibrils are responsible for the high tension stiffness and strength, while the hemicellulose-lignin-matrix makes for shear and compression stiffness by interconnecting the microfibrils. Different inclinations of the cellulose fibrils with respect to the cell axis enable the tree to react to different loading types. Crystalline cellulose shows an almost purely elastic, anisotropic mechanical behavior with brittle failure under tension. In contrast, the amorphous structure of hemicellulose and lignin is characterized by different deformation mechanisms. Sliding of the polymer chains including breaking and reconnection of hydrogen bonds results in a timedependent behavior [99]. The thereon released elastic energy is stored in the surrounding material (most likely in its cellulosic parts). Thus the time-dependent deformation is (almost) recoverable. The deformation behavior of the wood cell wall therefore consists of an elastic component and a viscoelastic component (up to a certain mechanical state, where plastic deformations and/or damage occur in addition). Further, the mechanical behavior of the polymer matrix materials is depending on temperature, especially because of the glass transition of the wood polymers (hemicelluloses and lignin) at a certain temperature, which is in addition depending on moisture content.

Being part of the molecular structure of wood, the bound water also strongly influences the stiffness and time-dependent behavior of wood. High levels of bound water concentration implicate a lowered stiffness and increased viscosity of wood, since water acts as a plasticizer [91]. Furthermore, a variable moisture content history results in an accelerated creep, a so called mechano-sorptive behavior [105].

Deformations of the cell wall material origin from mechanical loading, from changes in moisture content (as mentioned in Section 2.2.3), and from thermal expansion. Obviously, these different origins have to be considered in the material description.

2.5 Summary

In this chapter the theoretical basis was laid for the mathematical description of wood. Both transport behavior and mechanical behavior are predicated on processes and behavior on the molecular and cellular scale. The effective macroscopic behavior of wood in addition is strongly influenced by the structure and composition on all length scales as described in Section 2.1. Based thereon, a consistent macroscopic mathematical description for wood is derived in the following chapter.

Chapter 3

Macroscopic continuum description of wood

Although the behavior of wood and the underlying processes are best described on a small length scale as done in the previous chapter, the material wood is used for objects, constructions, and structures on a much larger scale. An approach that explains the system behavior in terms of the properties on the microscale, might be useful from the viewpoint of material science, but will meet difficulties when it comes to large scale systems. To overcome this problem, usually a macroscopic continuum approach is chosen, which is – superficially – not concerned with the internal structure of the material but deals with the properties of the system as a whole instead [60]. However, the continuum description of a material has to incorporate macroscopically relevant information from lower scales. This is especially important for a diversified material like wood.

The mathematical description of a material as a continuum is based on several differential equations. Starting point will be the basic physical laws for conservation of mass, momentum, momentum of momentum, and energy. In addition, constitutive equations are needed, which define the material behavior. Finally, initial conditions and boundary conditions (which include the geometry of the sample) define the individual problems.

In addition, the comprehensive set of equations for "wood" will be specialized for some important special cases at the end of this chapter. In the formulation of the according differential equations, simplifying assumptions will be made. These assumptions are accompanied by limits of applicability of the resulting sets of equations.

Across this thesis, the correct formulation and consideration of all strong and weak couplings will turn out to be of great importance, justifying a more extensive formulation compared to existing approaches in this field. In many cases experimentally observed material behavior can be explained on a physical basis. In addition, unphysical parameters stemming from a wrong (in most cases oversimplified) macroscopic set of equations are avoided. Due to the correct derivation of balance equations and constitutive relations all parameters have a clearly defined physical meaning.

3.1 Macroscopic balance equations

Irrespective of the considered material, the basic balance laws of physics apply at all times (as long as the continuum exists – e.g. macroscopic fracture is a structural problem which is not contained in a continuum description). For each system they consist of conservation of mass, balance of momentum, balance of momentum of momentum, and conservation of energy [60] [23]. In addition, the second law of thermodynamics must be satisfied.

In this chapter, a linearized approach is presented, i.e. no differentiation is made between reference \mathbf{x} and current configuration \mathbf{X} of the solid parts, therefore there is no need to differentiate between material and particulate derivatives. All balance equations are formulated for a unit volume. In this volume, each constituent *i* is assigned a mass density $\rho_i(\mathbf{x}, t)$, depending on space \mathbf{x} and time *t*. For a system made up of *n* constituents, the total density per unit volume $\rho(\mathbf{x}, t)$ is defined by

$$\rho(\mathbf{x},t) = \sum_{i=1}^{n} \rho_i(\mathbf{x},t).$$
(3.1)

Since the scope of this thesis is wood under conditions below the fiber saturation point, meaningful components of wood from a macroscopic point of view are

- solid (s), incorporating all immobile phases within a wood tissue,
- bound water (b), and
- water vapor (v).

This nonexhaustive enumeration of course may be extended, for example liquid water (l) for conditions above the fiber saturation point. For convenience, the mass concentrations of bound water c_b , (mass per volume of pure cell wall material) and water vapor, c_v (mass per volume of pure lumen) are introduced as

$$c_b \equiv \frac{\rho_b}{f_{\rm cwm}}, \qquad c_v \equiv \frac{\rho_v}{f_{\rm lum}},$$
(3.2)

with $f_{\rm cwm}$ and $f_{\rm lum}$ denoting the volume fractions of cell wall material and lumen, respectively.

3.1.1 Conservation of mass

For each constituent i of a material, its mass conservation can be written as [60]

$$\frac{\partial \rho_i}{\partial t} + \frac{\partial}{\partial \mathbf{x}} \cdot \mathbf{J}_i - \rho \kappa_i = 0, \tag{3.3}$$

with \mathbf{J}_i denoting the mass flux and κ_i denoting the mass supply rate for component *i* upon chemical reactions or phase changes. To satisfy conservation of mass for the whole system,

$$\sum_{i=1}^{n} \kappa_i = 0 \tag{3.4}$$
must hold. Specification of Eqs. (3.3) and (3.4) for wood yields two mass conservation equations for bound water and water vapor, reading as

$$\frac{\partial \rho_b}{\partial t} + \frac{\partial}{\partial \mathbf{x}} \cdot \mathbf{J}_b - \rho \kappa_b = 0, \tag{3.5}$$

$$\frac{\partial \rho_v}{\partial t} + \frac{\partial}{\partial \mathbf{x}} \cdot \mathbf{J}_v - \rho \kappa_v = 0.$$
(3.6)

with $\rho \kappa_b = -\rho \kappa_v \equiv \dot{c}$ accounting for changes in mass densities upon sorption, expressed by the sorption rate \dot{c} . In combination with Eq. (3.2), Eqs. (3.5) and (3.6) can thus be rewritten as

$$\frac{\partial(c_b f_{\text{cwm}})}{\partial t} + \frac{\partial}{\partial \mathbf{x}} \cdot \mathbf{J}_b - \dot{c} = 0, \qquad (3.7)$$

$$\frac{\partial (c_v f_{\text{lum}})}{\partial t} + \frac{\partial}{\partial \mathbf{x}} \cdot \mathbf{J}_v + \dot{c} = 0.$$
(3.8)

3.1.2 Balance of momentum

For static conditions, the balance of momentum for the system reads as

$$\frac{\partial}{\partial \mathbf{x}} \cdot \mathbf{\Sigma} + \rho \,\mathbf{g} = 0, \tag{3.9}$$

where Σ denotes the macroscopic stress tensor and **g** is the body force vector. Momentum supply due to the movement of water vapor and bound water is neglected.

3.1.3 Balance of moment of momentum

The balance of moment of momentum results in [23]

$$\Sigma - \Sigma^{\mathrm{T}} = 0, \tag{3.10}$$

The superscript T denotes the transpose of the according matrix. Eq. (3.10) implies that the macroscopic stress tensor is symmetric, i.e. that $\Sigma_{kl} = \Sigma_{lk}$, $k, l \in [1, 2, 3]$.

3.1.4 Conservation of energy

The conservation of energy may be expressed as

$$\frac{\mathrm{d}(\rho e)}{\mathrm{d}t} - \boldsymbol{\Sigma} : \frac{\mathrm{d}\mathbf{E}}{\mathrm{d}t} + \frac{\partial}{\partial\mathbf{x}} \cdot \mathbf{f} - \rho \, b + \frac{\partial}{\partial\mathbf{x}} \cdot \mathbf{J}_{\mathbf{b}} \, \overline{h}_{b} + \frac{\partial}{\partial\mathbf{x}} \cdot \mathbf{J}_{\mathbf{v}} \, h_{v} + \dot{c} \left(h_{v} - h_{b}\right) = 0, \quad (3.11)$$

where e is the specific internal energy, **E** is the (macroscopically observable) strain tensor, b is an external energy source per unit mass, **f** is the heat flux, and h_b and h_v are the specific enthalpies of bound water and water vapor, respectively. The term $(h_v - h_b)$ is the specific enthalpy of the phase transition of water from the bound state to the vapor state, while \overline{h}_b is the average enthalpy of bound water [106].

3.1.5 Clausius-Duhem inequality

The Clausius-Duhem inequality is a way to express the second law of thermodynamics, commonly used in continuum mechanics. It is useful to determine the admissibility of constitutive relations of a material. In differential form it reads as [23]

$$\frac{\mathrm{d}(\rho s)}{\mathrm{d}t} \ge -\frac{\partial}{\partial \mathbf{x}} \cdot \left(\frac{\mathbf{f}}{T}\right) + \frac{\rho b}{T} - \frac{\partial}{\partial \mathbf{x}} \cdot \mathbf{J}_{\mathbf{b}} \,\overline{s}_{b} - \frac{\partial}{\partial \mathbf{x}} \cdot \mathbf{J}_{\mathbf{v}} \,s_{v} - \dot{c} \,\frac{h_{v} - h_{b}}{T} \tag{3.12}$$

In Eq. (3.12), s denotes the specific entropy and T the thermodynamic (absolute) temperature.

3.2 Constitutive equations

The six field equations (3.7) - (3.9) and (3.11) cannot be solved since they don't contain information about the material yet. This comes in through so-called constitutive relations, connecting the variables in the field equations. It is worth being noticed that the constitutive relations are independent from size or shape of the sample or from the boundary conditions.

The independent field variables in the six balance equations are

- the mass concentration of bound water $c_b(\mathbf{x}, t)$,
- the mass concentration of water vapor $c_v(\mathbf{x}, t)$,
- the strain tensor $\mathbf{E}(\mathbf{x}, t)$, and
- the absolute temperature $T(\mathbf{x}, t)$.

The six independent components of the strain tensor \mathbf{E} can further be expressed as function of the displacement vector of the solid $\mathbf{u}_s(\mathbf{x},t) = (u_1, u_2, u_3)_s^{\mathrm{T}}(\mathbf{x},t)$. In continuum mechanics the infinitesimal strain theory is often used, approximating the strain tensor \mathbf{E} by Cauchy's strain tensor $\boldsymbol{\varepsilon}$ as

$$\mathbf{E} \approx \boldsymbol{\varepsilon} = \frac{1}{2} \left((\operatorname{grad} \mathbf{u}_s)^{\mathrm{T}} + \operatorname{grad} \mathbf{u}_s \right).$$
(3.13)

The infinitesimal strain theory is restricted to small displacements and small displacement gradients, i.e. $\|\mathbf{u}_s\| \ll 1$ and $\|\text{grad } \mathbf{u}_s\| \ll 1$.

The remaining dependent variables are

- the mass flux vector of bound water \mathbf{J}_b ,
- the mass flux vector of water vapor \mathbf{J}_v ,
- the stress tensor Σ ,
- the sorption rate \dot{c} ,
- the heat flux vector **f**, and

• the specific internal energy *e*.

In general, each of these variables may be a function of all independent field variables and their derivatives with respect to space and time. In addition they also may depend on time. This yields to the following set of constitutive equations:

$$\mathcal{F} = \mathcal{F}\left(c_b, \frac{\partial c_b}{\partial \mathbf{x}}, \frac{\partial c_b}{\partial t}, c_v, \frac{\partial c_v}{\partial \mathbf{x}}, \frac{\partial c_v}{\partial t}, \mathbf{E}, \frac{\partial \mathbf{E}}{\partial t}, T, \frac{\partial T}{\partial \mathbf{x}}, \frac{\partial T}{\partial t}, t\right),$$

$$\mathcal{F} \in \{\mathbf{J}_b, \mathbf{J}_v, \dot{c}, \mathbf{\Sigma}, \mathbf{f}, e\}.$$
(3.14)

Eq. 3.14 is in agreement with the principle of equipresence [60] that each independent variable should be present in all constitutive equations unless this is in contradiction to the second law of thermodynamics [see Eq. (3.12)].

Whereas the balance equations as presented in Section 3.1 are basic laws of physic and apply to each material, the constitutive relations refer to the characteristic properties of one particular material, in this case the material wood. As described in Chapter 2, wood exhibits differences in geometry and composition observed at the macro-, micro-, and ultra-structural scale. This results in wide variability of all macroscopic material properties associated with the constitutive equations, which should be accounted for in measurements and theoretical derivations of material properties of wood.

3.2.1 Mass fluxes of bound water and water vapor

As mentioned in Chapter 2, the main transport process of both bound water and water vapor under conditions below the fiber saturation point is diffusion. In general, diffusion is driven by gradients in chemical potential, which is a function of concentration, temperature and stress (pressure). Fick's first law of diffusion links a diffusive flux **J** of a substance and a corresponding gradient in chemical potential μ :

$$\mathbf{J} = -\mathbf{D}^{\mu} \cdot \frac{\partial \mu}{\partial \mathbf{x}},\tag{3.15}$$

with **D** denoting the diffusion tensor. The macroscopic (effective) fluxes \mathbf{J}_b and \mathbf{J}_v can be described using macroscopic (effective) diffusion tensors \mathbf{D}_b and \mathbf{D}_v . In general, these tensors depend on the state variables c_b , c_v , \mathbf{E} , and T.

Neglecting the dependence of chemical potential on temperature and stress, Fick's first law may also be written using directly a gradient in concentration:

$$\mathbf{J} = -\mathbf{D} \cdot \frac{\partial c}{\partial \mathbf{x}}.$$
(3.16)

This representation is prevalent in wood science. However, it might lead to problems under pronounced gradients in temperature.

3.2.2 Heat flux

Heat is transported in wood mainly by heat conduction. This is described by Fourier's law, linking a heat flux \mathbf{f} and a gradient in temperature T by the thermal conductivity

tensor \mathbf{K} :

$$\mathbf{f} = -\mathbf{K} \cdot \frac{\partial T}{\partial \mathbf{x}}.\tag{3.17}$$

The macroscopic (effective) thermal conductivity tensor of wood is in good approximation solely a function of bound water concentration c_b and temperature T.

3.2.3 Stress

The causes for (macroscopic) stress in wood are (macroscopic) strains, changes in bound water concentration and changes in temperature. Neglecting the latter (which are usually small compared to the other), the constitutive equation for stress may be written in the framework of microporoplasticity as [16]

$$\boldsymbol{\Sigma} = \mathbb{C} : \left(\mathbf{E} - \mathbf{E}^{\text{pl}} \right) - \mathbf{b}(p_b - p_{b,0}), \qquad (3.18)$$

where \mathbb{C} is the macroscopic stiffness tensor, \mathbf{E}^{pl} are the plastic strains, **b** is the Biot tensor, and p_b is the pressure in the bound water phase. $p_{b,0}$ denotes the initial bound water pressure. In general, both material properties (\mathbb{C} , **b**) are functions of bound water concentration, temperature, strain, and – in addition – time.

3.2.4 Sorption rate

As described in Chapter 2, sorption is the exchange process between bound water and water vapor. This process is driven by differences in chemical potential of the two phases. The time dependence of sorption presumably arises from two causes: first because of the transport process inside the cell wall (see Section 2.3.3) and second because of the time-dependent evolution of stress stemming from the volume changes accompanied with sorption (stress influences sorption because of the pressure-dependence of the chemical potential of bound water).

In addition, the equilibrium state between water vapor and bound water is dependent on loading history (again probably because of the pressure-dependence of chemical potential of bound water). In general, sorption may be expressed as

$$\dot{c} = \mathfrak{f}(c_b, T) \left[\mu_v(c_v, T) - \mu_b(c_b, T, \mathbf{E}) \right], \tag{3.19}$$

where the term in squared brackets is the difference in chemical potential between the two phases, while $\dot{\mathfrak{f}}(c_b, T)$ is a function representing the transport process in the cell wall. For the latter, a model is derived in Section 7.2 of this thesis.

3.2.5 Internal energy

The internal energy is the sum of all forms of energy intrinsic to the system. It may be divided into potential energy and kinetic energy, the first arises from motion of all particles (electrons, atoms, molecules,...) in the system, the latter includes all energies given by the mass of the system's components, for instance chemical energy, nuclear energy, and deformation energy. Internal energy is therefore a function of all state variables. In the balance equation (3.11), the differential of the internal energy per unit volume, $d(\rho e)$, is used. It may be written as

$$d(\rho e) = Td(\rho s) + \Sigma : d\mathbf{E}^{el} + \sum_{i=1}^{n} \mu_i dN_i, \qquad (3.20)$$

where \mathbf{E}^{el} is the elastic strain tensor, and $N_i = \rho_i / M_i$ is the number of molecules per volume, with M_i denoting the molar mass of component *i*. As introduced before, *s* is the specific entropy.

Under conditions, where the changes of the strain tensor **E** and the concentrations ρ_i are negligibly small, the differential of internal energy per unit unit volume may be written only as function of temperature T as

$$d(\rho e) = \rho \, de = \rho \left(\frac{\partial e}{\partial T}\right)_{V,N_i} dT = \rho \, c_V \, dT, \qquad (3.21)$$

where c_V is the specific heat capacity of wood at constant volume. It is a function of T and c_b [112].

3.3 Initial conditions

For each material point in the considered domain (i.e. inside the wood sample), the values of all field variables c_b , c_v , \mathbf{u} , and T at time t_0 must be specified as initial conditions. Usually, local near-equilibrium conditions are chosen at each point.

3.4 Boundary conditions

In addition to the geometry of the particular sample, the interaction of the sample on its surface with the surrounding has to be specified via boundary conditions. Several types of boundary conditions can be distinguished. The first one is the direct specification of state variables (Dirichlet boundary conditions):

$$c_b = \bar{c}_b, \quad c_v = \bar{c}_v, \quad T = T, \quad \mathbf{u} = \bar{\mathbf{u}}.$$
 (3.22)

The specification of the derivative of a state variable is called Neumann boundary condition. Especially a Neumann boundary condition equal to zero is of practical importance. In case of c_b , c_v , and T, this describes a perfectly dense and insulated macroscopic surface (symmetry planes), while in the mechanical problem this represents a free, unloaded surface. The according mathematical representations read as

$$\frac{\partial c_b}{\partial \mathbf{n}} = 0, \quad \frac{\partial c_v}{\partial \mathbf{n}} = 0, \quad \frac{\partial T}{\partial \mathbf{n}} = 0, \quad \frac{\partial \mathbf{u}}{\partial \mathbf{n}} = 0, \tag{3.23}$$

where \mathbf{n} is the normal vector of the surface.

Other possible boundary conditions consist in the direct specification of dependent variables. This reads as

$$\mathbf{J}_b = \bar{\mathbf{J}}_b, \quad \mathbf{J}_v = \bar{\mathbf{J}}_v, \quad \mathbf{f} = \bar{\mathbf{f}}, \quad \boldsymbol{\Sigma} = \boldsymbol{\Sigma}.$$
 (3.24)

It should be mentioned that the prescribed values may also depend on the state variables on the surface. For example at a surface that is in contact with air, interaction with the surrounding is limited to water vapor flux and heat flux. Usually, water vapor concentration and temperature are known in some distance from the sample surface, denoted in the following by c_v^0 and T^0 . The transport of water and energy towards the sample involves a combination of moisture diffusion and heat conduction as well as of air flow and convection, depending on conditions like surrounding air speed and surface roughness. If detailed modeling of these processes should be avoided, so-called film boundary conditions can be used instead as a simplified phenomenological description:

$$\bar{\mathbf{J}}_v = -k_v \left(c_v - c_v^0 \right) \,\mathbf{n},\tag{3.25}$$

$$\bar{\mathbf{f}} = -k_T \left(T - T^0\right) \mathbf{n},\tag{3.26}$$

with k_v and k_T denoting the film boundary coefficients for water vapor and temperature, respectively.

3.5 Special cases

If all constitutive equations (3.14) are known exactly, the field equations (3.7) - (3.9) and (3.11) in combination with the initial and boundary conditions yield the mathematical description of any process in a particular sample. However, often the components of the constitutive relations are not accessible in detail. In addition, solving the complete set of coupled differential field equations is a demanding task.

Fortunately, there are specific situations where some of the field variables are – at least in good approximation – constant. Hence, the field equations and constitutive equations get partly decoupled and the required number of equations reduces. As for experiments, the accurate monitoring of all variables at the same time is impossible, some of them are not even measurable. Thus, also in experiments usually only special cases are investigated.

In the following, several situations are presented where the mechanical and transport problems may be treated in a decoupled manner, accompanied by remarks regarding the used material properties.

3.5.1 Static conditions

Static conditions in an open thermodynamic system as wood imply that all derivations with respect to time equal zero. In addition, the external energy source in Eq. (3.11) is zero too, as are the gradients in concentration and temperature – no transport of energy and moisture occurs. Thus, only Eq. (3.9) has to be considered, in combination with Eq. (3.18) this yields

$$\frac{\partial}{\partial \mathbf{x}} \cdot \left[\mathbb{C} : \left(\mathbf{E} - \mathbf{E}^{\mathrm{pl}} \right) \right] + \rho \mathbf{g} = 0.$$
(3.27)

In this equation, the only material property is the stiffness tensor $\mathbb{C}(\rho_i, T)$. It can be derived either experimentally or theoretically based on the microstructural characteristics of the material. An according approach for the initial linear elastic response ($\mathbf{E}^{\text{pl}} = 0$) is given and validated in [44, 45, 46].

3.5.2 Time-dependent mechanical material behavior

Under constant climatic conditions as in the previous subsection and under negligence of the work term in the energy balance, the time-dependent evolution of stresses and strains may be described by Eq. (3.27) in good approximation. For this purpose, the timedependent relaxation tensor $\mathbb{R}(\rho_i, T, t)$ has to be determined. This is done in Chapter 9 of this thesis, again for loads below the limit of linear viscoelasticity¹.

3.5.3 Steady state conditions: temperature gradient

Again conditions are considered where all time derivatives vanish. In addition no relevant moisture transport occurs. The only process is heat conduction, caused by a superimposed gradient in temperature. Considering the constitutive relation (3.17), Eq. (3.11) may be written under negligence of the external volumetric heat sources as

$$\frac{\partial}{\partial \mathbf{x}} \cdot \left(\mathbf{K} \cdot \frac{\partial T}{\partial \mathbf{x}} \right) = 0. \tag{3.28}$$

The according thermal conductivity tensor K is derived theoretically in Chapter 4 of this thesis. A concurrent static mechanical problem can be calculated subsequently, using the temperature field resulting from Eq. (3.28) as input.

3.5.4 Steady state conditions: moisture gradient

The time derivatives of all field variables are zero again, in addition the heat flux is zero. The only transport process now is steady state moisture transport caused by a time-independent gradient in moisture content. As mentioned in Section 2.3.2, such conditions involve equilibrium of bound water and water vapor and a vanishing sorption rate. Thus only one mass balance equation is needed, leading in combination with Fick's law of diffusion (3.16) to

$$\frac{\partial}{\partial \mathbf{x}} \cdot \left(\mathbf{D} \cdot \frac{\partial c}{\partial \mathbf{x}} \right) = 0. \tag{3.29}$$

In this equation, c stands for an arbitrarily chosen value of water concentration (e.g. moisture content, bound water concentration, relative humidity), while **D** denotes the according diffusion tensor. A theoretical derivation of the moisture diffusion tensor under steady state conditions is given in Chapter 5 of this thesis.

Again a concurrent mechanical problem can be calculated subsequently, using the water concentration field resulting from Eq. (3.29) in combination with hygroexpansion coefficients as input.

¹The term "linear viscoelasticity" implies that the compliance of the material does not dependend on stress or strain. Accordingly, the Boltzmann superposition principle applies, allowing to describe the combined effect of different loadings at different time instances. Above a certain state of stress and strain, the time-dependent mechanical behavior of wood becomes more and more non-linear, this state is labeled as "limit of linear viscoelasticity".

3.5.5 Transient moisture transport

The last presented special case is that of transient moisture transport, when the concentrations of bound water and water vapor change with time. A changing moisture content also implies a shrinkage and swelling of the material. In principle, the thus according mechanical work has to be accounted for in conservation of energy. However, compared to the amount of energy resulting from sorption the mechanical work is relatively small and can thus be neglected in Eq. (3.11). To account for the influence of stress state on the equilibrium between the two water phases a suitable empirical model exists (Section 7.3). Thus the mechanical problem decouples from the transport problem, a separate treatment is possible.

Fig. 3.1 schematically shows the different transport processes in wood and also the interaction between wood and its ambiance on the microscopic scale. At this scale, the spatial separation of the two phases of water allows for a simple but physically correct representation of the processes occurring in wood subjected to a transient change in moisture content.



Figure 3.1: Illustration of the various time-dependent processes within wood, separated for the three state variables bound water concentration c_b , the water vapor concentration c_v and internal energy e.

The relevant state variables describing a transient moisture transport process are the bound water mass concentration c_b , the water vapor mass concentration c_v , and energy in terms of thermodynamic temperature T. Their temporal change is governed by three coupled differential equations:

$$\frac{\partial(c_b f_{\rm cwm})}{\partial t} + \frac{\partial}{\partial \mathbf{x}} \cdot \mathbf{J}_b - \dot{c} = 0, \qquad (3.30)$$

$$\frac{\partial (c_v f_{\text{lum}})}{\partial t} + \frac{\partial}{\partial \mathbf{x}} \cdot \mathbf{J}_v + \dot{c} = 0, \tag{3.31}$$

$$\frac{\mathrm{d}(\rho e)}{\mathrm{d}t} + \frac{\partial}{\partial \mathbf{x}} \cdot \mathbf{f} + \frac{\partial}{\partial \mathbf{x}} \cdot \mathbf{J}_b \,\overline{h}_b + \frac{\partial}{\partial \mathbf{x}} \cdot \mathbf{J}_v \,h_v + \dot{c} \left(h_v - h_b\right) = 0. \tag{3.32}$$

Compared to the other special cases, this formulation contains a larger number of material properties. An experimental determination of these properties is impossible, since they hardly can be controlled separately. In addition, analytical solutions for three coupled non-linear differential equations are not possible.

To overcome these deficiencies, in Chapter 8 of this thesis the material parameters are derived analytically, while in Chapter 9 a numerical solution of the problem is derived in the framework of the Finite Element Method. These tools enable the description of transient moisture transport in wood. Their successful operation is validated in Chapters 10 and 11.

Chapter 4

Multiscale model for thermal conductivity

This chapter covers the development and validation of a multiscale homogenization model for macroscopic transport properties of wood. The starting point is the intrinsic structural hierarchy of wood and its elementary constituents on the molecular scale as described in Section 2.1. Thereon the macroscopic material behavior of wood is derived by revisiting – in a mathematical way – the microstructure of wood.

Model validation rests on statistically and physically independent experiments: the macroscopic thermal conductivity values predicted by the multiscale homogenization model on the basis of tissue-independent ("universal") phase conductivity properties of hemicellulose, cellulose, lignin, and water (input data set I) for tissue-specific data (input data set II) are compared to corresponding experimentally determined tissue-specific conductivity values (experimental data set).

4.1 Introduction

In comparison to other building materials, wood exhibits a low thermal conductivity. The reason for that is the porous microstructure of the material, which is also responsible for the anisotropic macroscopic material behavior. Overall, the differences in geometry and composition observed at the macro-, micro-, and ultra-structural scale (see Chapter 2) result in wide variability of macroscopic material properties such as heat conductivities and moisture diffusivities.

In order to establish a model that can predict properties also for non-tested conditions, one has to start from tissue-independent material properties. In wood such properties can be found only on the molecular scale, where elementary constituents of wood can be identified. In order to derive macroscopic properties therefrom, one has to consider the entire hierarchical organization of clear (knot free) wood as presented in Chapter 2 and to account for the individual design of structural features in particular samples. This is done via a multiscale homogenization model in the present work, which allows to calculate macroscopic properties of wood by means of an analytical approach resulting in closed form solutions. Since the structure of the governing constitutive equations is analogous for thermal conduction and steady state moisture diffusion, the model developed herein is also applied to diffusion in the following chapter.

4.2 Fundamentals of continuum micromechanics

Continuum micromechanics¹ is the analysis of heterogeneous materials on the level of the single phases that constitute this material. A material is understood as a macrohomogeneous, but micro-heterogeneous body filling a representative volume element (RVE) with characteristic length ℓ , $\ell \gg d$, d standing for the characteristic length of inhomogeneities within the RVE (see Fig. 4.1), and $\ell \ll L$, L standing for the characteristic length of a structure built up by the material defined on the RVE.

In general, the microstructure within the RVE is so complicated that it cannot be described in complete detail. Therefore, quasi-homogeneous sub-domains with known physical properties (such as volume fractions and thermal conductivities) are reasonably chosen. They are called material phases. The homogenized behavior of the overall material, i.e. the relation between temperature gradients acting on the boundary of the RVE and resulting (average) thermal fluxes in case of heat transport, can then be estimated from the behavior of the homogeneous phases (representing the inhomogeneities within the RVE), their volume fractions within the RVE, their characteristic shapes, and their interactions.

Originally these concepts were formulated for the equivalent mechanical problem, aiming at estimation of homogenized stiffness properties. Due to the similarity of the governing differential equations, the approach is also applicable to transport processes. Based on solutions of matrix–inclusion problems, an estimate for the homogenized thermal conductivity tensor \mathbf{K}^{hom} of the material reads as [15]:

$$\mathbf{K}^{\text{hom}} = \left\{ \sum_{r} f_{r} \,\mathbf{K}_{r} \cdot \left[\mathbf{I} + \mathbf{P}_{r}^{0} \cdot \left(\mathbf{K}_{r} - \mathbf{K}^{0} \right) \right]^{-1} \right\} \cdot \left\{ \sum_{s} f_{s} \left[\mathbf{I} + \mathbf{P}_{s}^{0} \cdot \left(\mathbf{K}_{s} - \mathbf{K}^{0} \right) \right]^{-1} \right\}^{-1},$$

$$(4.1)$$

where \mathbf{K}_r and f_r denote the thermal conductivity tensor and the volume fraction of phase r, respectively, and \mathbf{I} is the second order unity tensor. The two sums are taken over all phases of the heterogeneous material in the RVE. The second order **P**-tensor or Hill tensor, \mathbf{P}_r^0 , accounts for the characteristic shape of phase r in a matrix with thermal conductivity tensor \mathbf{K}^0 . Two different formations of the phases can be mathematically reproduced: For \mathbf{K}^0 corresponding to one of the phase thermal conductivity tensors (Mori-Tanaka scheme), a composite material is represented (continuous matrix with inclusions); for $\mathbf{K}^0 = \mathbf{K}^{\text{hom}}$ (self-consistent scheme), a dispersed arrangement of the phases is considered.

¹The term 'micromechanics' is rooted in history and is applied in conjunction with the homogenization of elasticity properties as well as that of transport properties.

In mechanical analysis, the Hill tensor \mathbf{P}_r^0 is conventionally derived from Eshelby's solution for mechanical matrix-inclusion problems. The application of this solution to transport processes and the derivation of the respective second order Hill Tensor for spherical inclusions is presented in [15] and [16]. Its generalization to ellipsoidal inclusions with ellipsoidal radii a_1 , a_2 , and a_3 results in the following formulation for its components [20]:

$$P_{ell,ij}^{0} = \frac{1}{4\pi} \int_{-1}^{+1} \int_{0}^{2\pi} \xi_{i} \xi_{j} \left(K_{kl}^{0} \xi_{k} \xi_{l} \right)^{-1} d\hat{\varphi} d\hat{\xi}_{3}, \qquad i, j, k, l \in [1, 2, 3], \qquad (4.2)$$

with

$$\xi_1 = \frac{\hat{\xi}_1}{a_1} = \frac{\sqrt{1 - \hat{\xi}_3^2 \cos \hat{\varphi}}}{a_1}, \qquad \xi_2 = \frac{\hat{\xi}_2}{a_2} = \frac{\sqrt{1 - \hat{\xi}_3^2 \sin \hat{\varphi}}}{a_2}, \qquad \xi_3 = \frac{\hat{\xi}_3}{a_3}. \tag{4.3}$$

Certainly this formulation covers the special cases of spherical inclusions $(a_1 = a_2 = a_3)$ as well as cylindrical inclusions (for example $a_1 = \infty$).

If a single phase exhibits a heterogeneous microstructure itself, its behavior can be estimated by introduction of an RVE within this phase, with dimensions $\ell_2 \leq d$, comprising again smaller phases with characteristic length $d_2 \ll \ell_2$, and so on (see Fig. 4.1). This procedure is continued until a scale is reached, on which the properties of the phases are all known and independent of the particular sample for the considered group of materials.



Figure 4.1: Multiscale homogenization

This leads to a multiscale homogenization scheme. A hierarchically structured material like wood of course suggests the use of such a homogenization scheme.

4.3 Thermal conductivities of the elementary components of wood

Considering the hierarchical organization of wood (see Section 2.1), sample-independent phases with "universal" properties inherent to all wood species may be identified only at an observation scale below the cell wall. Therefore, like it is done in Hofstetter et al. [44] for mechanical properties, its components (cellulose, hemicellulose, lignin, extractives, inorganic compounds, and water) are lumped into tissue-independent phases, characterized by different thermal properties. • Water and wood extractives: The term "wood extractives" covers a large number of different compounds, which can be extracted from wood by means of organic solvents [25]. They are generally in the solute state, which motivates their common treatment with water in one phase, indicated by the subscript H₂Oext. Water in the cell wall is in a bound state, resulting in a higher density and probably also a higher thermal conductivity of water. However, applicable values for bound water properties are not known to the author, therefore the values of free water were taken, which are tabulated in steam tables (e.g. [33]). Fitting a polynomial to these thermal conductivity values for temperatures between the freezing and the boiling point at normal pressure results in:

$$\lambda_{\rm H_2O} = -0.7282 + 7.299 \times 10^{-3} T - 9.454 \times 10^{-6} T^2 \quad [W/(m\,{\rm K})], \qquad (4.4)$$

where T denotes the actual temperature in [K]. Water is of course a thermally isotropic material, so that the thermal conductivity does not depend on the spatial direction of the temperature gradient.

- Hemicellulose: Hemicellulose is assumed to exhibit thermally isotropic material behavior as well. Its thermal conductivity is set equal to the value of glassy glucose at 20 °C, which amounts to $\lambda_{\text{hemcel}} = 0.34 \text{ W/(m K)}$ [31].
- Lignin: Also this component is assumed to show a thermally isotropic material behavior. Values for the thermal conductivity of pure lignin have not been measured yet. Therefore the thermal conductivity is back-calculated from the corresponding characteristic value of ARBOFORM[®] F45 nature [70], which is a thermoplastic material, with lignin occupying about 70 % of the dry volume. Additional natural particles make up the rest of the composite. A typical thermal conductivity of ARBOFORM[®] is $\lambda_{\text{ARBOFORM}} = 0.384 \text{ W/(m K)}$, measured at a water content of 6 % [70].

The thermal behavior of ARBOFORM[®] can be estimated from that of its constituents with a Mori-Tanaka scheme, considering lignin as continuous matrix, and the natural particles and water as inclusions. The thermal conductivities can be suitably chosen as $\lambda_{\text{part}} = 0.34 \text{ W/(m K)}$ for the natural particles (equal to the value of hemicellulose), and $\lambda_{\text{H}_2\text{O}} = 0.60 \text{ W/(m K)}$ for water (see Eq. (4.4), T = 293.15 K). Therewith the estimated thermal conductivity tensor of ARBOFORM[®] is

$$\mathbf{K}_{\text{ARBOFORM}}^{\text{MT}} = \left\{ f_{\text{lig}} \mathbf{K}_{\text{lig}} + \sum_{r} f_{r} \mathbf{K}_{r} \cdot \left[\mathbf{I} + \mathbf{P}_{\text{sph}}^{\text{lig}} \cdot (\mathbf{K}_{r} - \mathbf{K}_{\text{lig}}) \right]^{-1} \right\} \cdot \left\{ f_{\text{lig}} \mathbf{I} + \sum_{s} f_{s} \left[\mathbf{I} + \mathbf{P}_{\text{sph}}^{\text{lig}} \cdot (\mathbf{K}_{s} - \mathbf{K}_{\text{lig}}) \right]^{-1} \right\}^{-1}, \quad (4.5)$$
$$r, s \in [\text{part}, \text{H}_{2}\text{O}],$$

with volume fractions, taking into account the water content of 6%,

$$f_{\text{lig}} = \frac{0.70}{1+0.06} = 0.660,$$

$$f_{\text{part}} = \frac{0.30}{1+0.06} = 0.283,$$

$$f_{\text{H}_2\text{O}} = \frac{0.06}{1+0.06} = 0.057,$$

(4.6)

and with

$$\mathbf{K}_r = \lambda_r \mathbf{I}, \quad r \in [\text{lig, part, H}_2\text{O}, \text{ARBOFORM}].$$
 (4.7)

Solving Eq. (4.5) for the thermal conductivity of lignin, λ_{lig} , which is the only unknown variable, the value for dry lignin is gained as

$$\lambda_{\rm lig} = 0.39 \,{\rm W/(m \, K)}.$$
 (4.8)

Cellulose: The fourth tissue-independent component is cellulose. Although the thermal conductivity of cellulose insulations is well documented in literature, no values for the material cellulose itself are available. In order to estimate the thermal conductivities of partly crystalline cellulose as it is found in wood from these values, empirical relations derived from stretched polymers are employed, assuming similarity of the thermal behavior of partly crystalline cellulose and partly stretched polymers. Stretching of an amorphous polymer results in partial alignment of the polymer chains, so that structural and, in consequence, thermo-mechanical anisotropy of the material is introduced. Eiermann [19] proposes an empirical equation to relate the thermal conductivity of the unstretched isotropic polymer, λ^{iso}, to its corresponding properties parallel and perpendicular to the stretching direction, λ^{||} and λ[⊥], respectively:

$$\frac{3}{\lambda^{\rm iso}} = \frac{1}{\lambda^{\parallel}} + \frac{2}{\lambda^{\perp}}.\tag{4.9}$$

Analogously also anisotropy of the thermal expansion behavior is introduced by extensive stretching of polymers. Relations between the anisotropy ratios in thermal conductivity and linear thermal expansion coefficients were again formulated by [19]:

$$\frac{\lambda^{\text{iso}}}{\lambda^{\parallel}} = 0.8 \left(\frac{\alpha^{\parallel}}{\alpha^{\text{iso}}}\right) + 0.2, \tag{4.10}$$

$$\frac{\lambda^{\text{iso}}}{\lambda^{\perp}} = 0.8 \left(\frac{\alpha^{\perp}}{\alpha^{\text{iso}}}\right) + 0.2, \tag{4.11}$$

where α^{\parallel} and α^{\perp} denote thermal expansion coefficients parallel and perpendicular to the fiber direction. α^{iso} is the expansion coefficient of the unstretched (isotropic) polymer.

Assuming that the partial alignment of polymer chains upon stretching has a similar effect on the thermal behavior of amorphous polymers as the partial alignment of glucose chains in partly crystalline cellulose, Eqs. (4.9)-(4.11) can be applied to

wood cellulose. The thermal conductivity of amorphous cellulose is set equal to the value of glassy glucose, i.e. $\lambda_{cel}^{iso} = 0.34 \,\mathrm{W/(m\,K)}$, as it was done for hemicellulose. Thermal expansion coefficients of cellulose are known both parallel and perpendicular to the direction of the glucose chains. They amount to $\alpha_{cel}^{\parallel} = 0.60 \times 10^{-5} \,\mathrm{1/K}$ in the longitudinal direction and to $\alpha_{cel}^{\perp} = 5.30 \times 10^{-5} \,\mathrm{1/K}$ in the transverse one for partly crystalline wood cellulose [47]. Inserting Eqs. (4.10) and (4.11) in (4.9) and solving for $\lambda_{cel}^{\parallel}$ and λ_{cel}^{\perp} , respectively, yields

$$\lambda_{\rm cel}^{\parallel} = \frac{10 \,\alpha_{\rm cel}^{\perp} + 5 \,\alpha_{\rm cel}^{\parallel}}{2 \,\alpha_{\rm cel}^{\perp} + 13 \,\alpha_{\rm cel}^{\parallel}} \lambda_{\rm cel}^{\rm iso} = = 3.0435 \,\lambda_{\rm cel}^{\rm iso} = 3.0435 \times 0.34 \,\mathrm{W/(m\,K)} = 1.04 \,\mathrm{W/(m\,K)}, \qquad (4.12)$$

$$\lambda_{\rm cel}^{\perp} = \frac{10 \,\alpha_{\rm cel}^{\perp} + 5 \,\alpha_{\rm cel}^{\parallel}}{14 \,\alpha_{\rm cel}^{\perp} + 1 \,\alpha_{\rm cel}^{\parallel}} \,\lambda_{\rm cel}^{\rm iso} = = 0.7487 \,\lambda_{\rm cel}^{\rm iso} = 0.7487 \times 0.34 \,\mathrm{W/(m\,K)} = 0.26 \,\mathrm{W/(m\,K)}.$$
(4.13)

Assuming a reference frame in which axis 3 is aligned with the fiber direction, the resulting thermal conductivity tensor shows the following non-zero components: $K_{\text{cel},33} = \lambda_{\text{cel}}^{\parallel}$ and $K_{\text{cel},11} = K_{\text{cel},22} = \lambda_{\text{cel}}^{\perp}$.

Air: Since heat transport takes place also in the air filling the cell lumens, (moist) air constitutes another (tissue-independent) phase in the micromechanical model. Since the thermal conductivities of air and water vapor are very similar, they are not treated as separate phases, and the influence of the water vapor content on the overall thermal conductivity of air is neglected. Further, radiative convective or diffusive heat transfer within the cell lumens is not accounted for in this model for thermal conduction – the first two processes are negligible small due to the relatively low temperature level and the small temperature differences within one lumen, the latter is described by another process (flux of water vapor, see Chapter 3). Based on experimental results [52], the (isotropic) thermal conductivity of air is approximated by a polynomial depending on temperature:

$$\lambda_{\rm air} = 3.102 \times 10^{-4} + 9.500 \times 10^{-5} T - 2.917 \times 10^{-8} T^2 \quad [W/(m \, {\rm K})], (4.14)$$

with T as absolute temperature in [K].

Inorganic compounds such as, e.g., ash are only found in traces of typically 0.1 - 0.5 %. Given, in addition, their presumably similarly thermal conductivity compared to the other phases (for example $\lambda_{ash} = 0.14 - 0.31 \text{ W/(m K)}$ [84]), they hardly affect the thermal properties of wood at the macroscopic scale. Hence, they are not regarded in the model.

The obtained thermal conductivities of the remaining phases are summarized in Table 4.1.

Phase	Material behavior	$\lambda [{\rm W}/({\rm mK})]$
hemicellulose	isotropic	0.34
lignin	isotropic	0.39
water $+$ extractives	isotropic	$\lambda_{\rm H_2O}$, see Eq. (4.4)
lumen, vessel	isotropic	λ_{air} , see Eq. (4.14)
		$K_{ij} [W/(m K)]$
cellulose	transversely isotropic	$K_{\rm cel,11} = 0.26$
		$K_{\rm cel,22} = 0.26$
		$K_{\rm cel,33} = 1.04$

Table 4.1: Input data set I: 'Universal' phase thermal conductivity values

4.4 Definition of the multiscale homogenization model

Recalling the microstructure of wood as described in Section 2.1, the interaction of elementary components is considered in eight homogenization steps on six hierarchical levels, see Fig. 4.2. All steps are described in detail in the following subsections.

4.4.1 Step I: Polymer network

In the first homogenization step, an RVE of polymer network with 8–20 nm characteristic length is defined (see Fig. 4.2(I)). The polymer network is composed of hemicellulose, lignin, and water. These components are intimately mixed, occupying the volume fractions $\tilde{f}_{\text{hemcel}}$, \tilde{f}_{lig} and $\tilde{f}_{\text{H}_2\text{Oext}}$, with $\tilde{f}_{\text{hemcel}} + \tilde{f}_{\text{lig}} + \tilde{f}_{\text{H}_2\text{Oext}} = 1$. Within the network, the polymers and the water are mixed in a disordered manner. Hence a selfconsistent scheme with inclusions of spherical shape is used. Thus, in order to estimate the thermal conductivity of the polymer network, $\mathbf{K}_{\text{poly}}^{\text{SC}}$, Eq. (4.1) is specified for three (spherical) inclusion phases, i.e. for $r, s \in [\text{hemcel}, \text{ lig}, \text{H}_2\text{Oext}]$, for $\mathbf{K}^0 = \mathbf{K}_{\text{poly}}^{\text{SC}}$, and for $\mathbf{P}_{\text{hemcel}}^0 = \mathbf{P}_{\text{lig}}^0 = \mathbf{P}_{\text{H}_2\text{Oext}}^0 = \mathbf{P}_{\text{sph}}^{\text{poly}}$, resulting in

$$\mathbf{K}_{\text{poly}}^{\text{SC}} = \left\{ \sum_{r} \tilde{f}_{r} \mathbf{K}_{r} \cdot \left[\mathbf{I} + \mathbf{P}_{\text{sph}}^{\text{poly}} \cdot \left(\mathbf{K}_{r} - \mathbf{K}_{\text{poly}}^{\text{SC}} \right) \right]^{-1} \right\} \cdot \left\{ \sum_{s} \tilde{f}_{s} \left[\mathbf{I} + \mathbf{P}_{\text{sph}}^{\text{poly}} \cdot \left(\mathbf{K}_{s} - \mathbf{K}_{\text{poly}}^{\text{SC}} \right) \right]^{-1} \right\}^{-1}, \\ r, s \in [\text{hemcel, lig, H}_{2}\text{Oext}],$$

$$(4.15)$$

with $\mathbf{K}_{\text{hemcel}}$, \mathbf{K}_{lig} , and $\mathbf{K}_{\text{H}_2\text{Oext}}$ according to Table 4.1. The non-zero components of the symmetric tensor $\mathbf{P}_{\text{sph}}^{\text{poly}}$ read as follows:

$$P_{\rm sph,11}^{\rm poly} = P_{\rm sph,22}^{\rm poly} = P_{\rm sph,33}^{\rm poly} = 1/\left(3 \, K_{\rm poly,11}^{\rm SC}\right). \tag{4.16}$$

Since $K_{\text{poly},11}^{\text{SC}} = K_{\text{poly},22}^{\text{SC}} = K_{\text{poly},33}^{\text{SC}}$ is the only unknown variable, the implicit Eq. (4.15) can be solved directly.



Figure 4.2: Six-level homogenization procedure for thermal conductivity of wood

4.4.2 Step II: Cell wall material

In the next homogenization step, the conductivity tensor of the cell wall material is determined. A distinction of the different layers of the cell wall is not made. Mean values of the chemical composition and an average microfibril angle of 20° [45] are considered instead. An RVE with a characteristic length of 0.5–1 µm is defined. Therein, circular cylindrical inclusions representing cellulose fibers (with volume fraction f_{cel}), exhibiting typical diameters of 20–100 nm, are embedded in a contiguous polymer matrix (with volume fraction $f_{poly} = 1 - f_{cel}$). The behavior of such a composite material can be calculated by a Mori-Tanaka scheme. Thus, in order to estimate the thermal conductivity of the cell wall material, \mathbf{K}_{cwm}^{MT} , Eq. (4.1) is specified for one (right circular cylindrical) inclusion phase, i.e. for $r, s \in$ [cel, poly], for $\mathbf{K}^0 = \mathbf{K}_{poly}^{SC}$ from Eq. (4.15), and for $\mathbf{P}_{cel}^0 = \mathbf{P}_{circcyl}^{poly}$, resulting in

$$\mathbf{K}_{\text{cwm}}^{\text{MT}} = \left\{ f_{\text{poly}} \mathbf{K}_{\text{poly}}^{\text{SC}} + f_{\text{cel}} \mathbf{K}_{\text{cel}} \cdot \left[\mathbf{I} + \mathbf{P}_{\text{circcyl}}^{\text{poly}} \cdot \left(\mathbf{K}_{\text{cel}} - \mathbf{K}_{\text{poly}}^{\text{SC}} \right) \right]^{-1} \right\} \cdot \left\{ f_{\text{poly}} \mathbf{I} + f_{\text{cel}} \left[\mathbf{I} + \mathbf{P}_{\text{circcyl}}^{\text{poly}} \cdot \left(\mathbf{K}_{\text{cel}} - \mathbf{K}_{\text{poly}}^{\text{SC}} \right) \right]^{-1} \right\}^{-1},$$
(4.17)

with \mathbf{K}_{cel} according to Table 4.1. The non-zero components of the symmetric tensor $\mathbf{P}_{circcyl}^{poly}$ read as follows:

$$P_{\text{circcyl},11}^{\text{poly}} = P_{\text{circcyl},22}^{\text{poly}} = 1/\left(2K_{\text{poly},11}^{\text{SC}}\right).$$

$$(4.18)$$

The inclination of the cellulose fibers and, thus, of the principal material directions of the cell wall material in relation to the cell axis is implemented by rotation of the conductivity tensor $\mathbf{K}_{\text{cwm}}^{\text{MT}}$.

4.4.3 Step III(a) / Step III(b): Earlywood, latewood

In homogenization steps III(a) and III(b), the thermal conductivities of the cellular structures in earlywood and latewood – made up of wood tracheids, and, in hardwood samples, also of parenchyma cells and fibers – are calculated. All of these cells show similar dimensions and properties and, thus, can be treated together. The cell lumens, which show rectangular or polygonal cross sections and a strongly elongated shape aligned in the longitudinal direction, are approximated by ellipsoids in the model. The behavior of such a material is again suitably estimated by a Mori-Tanaka scheme. For earlywood, the RVE is defined at 100–150 µm characteristic length. It contains ellipsoidal pores with characteristic diameters of 10–50 µm, representing the cell lumens, embedded in a contiguous matrix built up by the cell wall material of homogenization step II (Eq. (4.17)). The volume fractions occupied by these two phases are \hat{f}_{lum} and \hat{f}_{cwm} , $\hat{f}_{lum} + \hat{f}_{cwm} = 1$. In order to formulate a Mori-Tanaka scheme for the estimation of the thermal conductivity of earlywood, \mathbf{K}_{early}^{MT} , Eq. (4.1) is specified for one (ellipsoidal) inclusion phase, and the cell wall matrix, i.e. for $r, s \in [lum, cwm]$, for $\mathbf{K}^0 = \mathbf{K}_{cwm}^{MT}$ from Eq. (4.17), and

for $\mathbf{P}_{\text{lum}}^0 = \mathbf{P}_{\text{ell,early}}^{\text{cwm}}$, resulting in

$$\mathbf{K}_{\text{early}}^{\text{MT}} = \left\{ \hat{f}_{\text{cwm}} \mathbf{K}_{\text{cwm}}^{\text{MT}} + \hat{f}_{\text{lum}} \mathbf{K}_{\text{air}} \cdot \left[\mathbf{I} + \mathbf{P}_{\text{ell,early}}^{\text{cwm}} \cdot \left(\mathbf{K}_{\text{air}} - \mathbf{K}_{\text{cwm}}^{\text{MT}} \right) \right]^{-1} \right\} \cdot \left\{ \hat{f}_{\text{cwm}} \mathbf{I} + \hat{f}_{\text{lum}} \left[\mathbf{I} + \mathbf{P}_{\text{ell,early}}^{\text{cwm}} \cdot \left(\mathbf{K}_{\text{air}} - \mathbf{K}_{\text{cwm}}^{\text{MT}} \right) \right]^{-1} \right\}^{-1}, \quad (4.19)$$

with \mathbf{K}_{air} according to Table 4.1. The components of the tensor $\mathbf{P}_{ell,early}^{cwm}$ are calculated from Eq. (4.2) with lumen diameters derived subsequently in Subsection 4.5.2.

The homogenized thermal conductivity tensor of latewood, $\mathbf{K}_{\text{late}}^{\text{MT}}$, follows from substitution of 'early' by 'late', and of ' \hat{f}_r ' by ' \check{f}_r ' in Eq. (4.19). The components of the tensor $\mathbf{P}_{\text{ell,late}}^{\text{cwm}}$ follow (as for earlywood) from Eq. (4.2) by use of the lumen diameters according to Subsection 4.5.2.

4.4.4 Step III(c): Ray cell material

Within an RVE of ray cell material with 50–500 µm characteristic length, ellipsoidal pores oriented in the radial direction with characteristic diameters of 5–15 µm, representing the ray cell lumens, are embedded in a contiguous matrix built up by the cell wall material of homogenization step II (Eq. 4.17). The slight difference in chemical composition between ray cells and the longitudinally oriented cells is neglected, but the different main microfibril orientation in ray cells, which is now parallel to the ray cell axis, is accounted for. The homogenization procedure is similar to homogenization steps III(a) and III(b), but the main axis of the pores and of the cellulose fibers in the cell wall is now oriented in radial direction. The volume fractions occupied by the two phases are $\dot{f}_{\rm lum}$ and $\dot{f}_{\rm cwm}$, $\dot{f}_{\rm lum} + \dot{f}_{\rm cwm} = 1$. Using again a Mori-Tanaka scheme for the estimation of the thermal conductivity of the ray cells, $\mathbf{K}_{\rm ray}^{\rm MT}$, Eq. (4.1) is specified for one (ellipsoidal) inclusion phase as the ray cell lumens, and one cell wall matrix, i.e. for $r, s \in [\text{lum}, \text{ cwm}]$, for $\mathbf{K}_{\rm air}$ according to Table 4.1, for $\mathbf{K}^0 = \mathbf{K}_{\rm cwm,rot}^{\rm MT}$ according to Eq. (4.21), and for $\mathbf{P}_{\rm lum}^0 = \mathbf{P}_{\rm ell,ray}^{\rm cwm}$, resulting in

$$\mathbf{K}_{\mathrm{ray}}^{\mathrm{MT}} = \left\{ \dot{f}_{\mathrm{cwm}} \mathbf{K}_{\mathrm{cwm}}^{\mathrm{MT}} + \dot{f}_{\mathrm{lum}} \mathbf{K}_{\mathrm{air}} \cdot \left[\mathbf{I} + \mathbf{P}_{\mathrm{ell,ray}}^{\mathrm{cwm}} \cdot \left(\mathbf{K}_{\mathrm{air}} - \mathbf{K}_{\mathrm{cwm}}^{\mathrm{MT}} \right) \right]^{-1} \right\} \cdot \left\{ \dot{f}_{\mathrm{cwm}} \mathbf{I} + \dot{f}_{\mathrm{lum}} \left[\mathbf{I} + \mathbf{P}_{\mathrm{ell,ray}}^{\mathrm{cwm}} \cdot \left(\mathbf{K}_{\mathrm{air}} - \mathbf{K}_{\mathrm{cwm}}^{\mathrm{MT}} \right) \right]^{-1} \right\}^{-1},$$
(4.20)

with

$$K_{\text{cwm,rot,11}}^{\text{MT}} = K_{\text{cwm,33}}^{\text{MT}},$$

$$K_{\text{cwm,rot,22}}^{\text{MT}} = K_{\text{cwm,rot,33}}^{\text{MT}} = K_{\text{cwm,11}}^{\text{MT}},$$

$$K_{\text{cwm,rot,ij}}^{\text{MT}} = 0 \quad \text{for} \quad i \neq j.$$

$$(4.21)$$

The components of the tensor $\mathbf{P}_{\text{ell,ray}}^{\text{cwm}}$ can again be calculated with Eq. (4.2), this time with the lumen diameters according to Subsection 4.5.2.

4.4.5 Step IV: Hardwood with vessels

In softwood tissues, all cells oriented in longitudinal direction show similar dimensions. In hardwood species, however, the vessels constitute additional cells at a larger length scale, making a fourth homogenization step necessary. Because of the predominant location of vessels in earlywood, vessels are only considered in this tissue type (and not in latewood) in the model. A further distinction regarding ring porous hardwood and diffusive porous hardwood is not made.

Within an RVE of hardwood with vessels showing 1–2 mm characteristic length, cylindrical pores oriented in longitudinal direction with characteristic diameters of 200–500 µm, representing the vessels, are embedded in a contiguous matrix built up by earlywood of homogenization step III(a) [Eq. (4.19)]. The volume fractions occupied by these two phases are \bar{f}_{ves} and \bar{f}_{early} , $\bar{f}_{\text{ves}} + \bar{f}_{\text{early}} = 1$. Using again a Mori-Tanaka scheme for the estimation of the thermal conductivity of hardwood with vessels, $\mathbf{K}_{\text{hard}+\text{ves}}^{\text{MT}}$, Eq. (4.1) is specified for one (cylindrical) inclusion phase as the vessels, and the earlywood matrix, i.e. for $r, s \in$ [ves, early], for $\mathbf{K}_{\text{ves}} = \mathbf{K}_{\text{air}}$ according to Table 4.1, for $\mathbf{K}^0 = \mathbf{K}_{\text{early}}^{\text{MT}}$ according to Eq. (4.19), and for $\mathbf{P}_{\text{ves}}^0 = \mathbf{P}_{\text{circcyl}}^{\text{early}}$, resulting in

$$\mathbf{K}_{\text{hard}+\text{ves}}^{\text{MT}} = \left\{ \bar{f}_{\text{early}} \mathbf{K}_{\text{early}}^{\text{MT}} + \bar{f}_{\text{ves}} \mathbf{K}_{\text{ves}} \cdot \left[\mathbf{I} + \mathbf{P}_{\text{circcyl}}^{\text{early}} \cdot \left(\mathbf{K}_{\text{ves}} - \mathbf{K}_{\text{early}}^{\text{MT}} \right) \right]^{-1} \right\} \cdot \left\{ \bar{f}_{\text{early}} \mathbf{I} + \bar{f}_{\text{ves}} \left[\mathbf{I} + \mathbf{P}_{\text{circcyl}}^{\text{early}} \cdot \left(\mathbf{K}_{\text{ves}} - \mathbf{K}_{\text{early}}^{\text{MT}} \right) \right]^{-1} \right\}^{-1}.$$
(4.22)

The components of the tensor $\mathbf{P}_{\text{circcyl}}^{\text{early}}$ can be calculated by specializing Eq. (4.2) for circular cylindrical inclusions, i.e. for $a_1 = a_2 = 1$, $a_3 = \infty$.

4.4.6 Step V: Annual rings

The arrangement in layers of earlywood and latewood in the annual rings at a length scale of about 5–10 mm is taken into account by rules of mixture: While the layers are connected in series in radial direction, they are arranged in parallel in tangential and longitudinal direction. Therefore, the homogenized thermal conductivities of the annual ring material in relation to its principal material directions can be written as:

$$K_{\text{ann,11}}^{\text{S/P}} = \left(\ddot{f}_{(\text{hard}+\text{ves})} / K_{\text{hard}+\text{ves,11}}^{\text{MT}} + \ddot{f}_{\text{late}} / K_{\text{late,11}}^{\text{MT}} \right)^{-1},$$

$$K_{\text{ann,22}}^{\text{S/P}} = \ddot{f}_{(\text{hard}+\text{ves})} K_{\text{hard}+\text{ves,22}}^{\text{MT}} + \ddot{f}_{\text{late}} K_{\text{late,22}}^{\text{MT}},$$

$$K_{\text{ann,33}}^{\text{S/P}} = \ddot{f}_{(\text{hard}+\text{ves})} K_{\text{hard}+\text{ves,33}}^{\text{MT}} + \ddot{f}_{\text{late}} K_{\text{late,33}}^{\text{MT}}.$$
(4.23)

All homogenization steps till step V result in orthotropic material behavior with respect to the three principal material axes of wood. This means that off-diagonal components of $\mathbf{K}_{\text{hard}+\text{ves}}^{\text{MT}}$ and $\mathbf{K}_{\text{late}}^{\text{MT}}$ are equal to zero. In consequence, also the off-diagonal components of $\mathbf{K}_{\text{ann}}^{\text{S/P}}$ vanish when represented in relation to the principal material directions, resulting again in an orthotropic material behavior expressed by the following structure of the conductivity tensor:

$$\mathbf{K}_{\rm ann}^{\rm S/P} = \begin{bmatrix} K_{\rm ann,11}^{\rm S/P} & 0 & 0\\ 0 & K_{\rm ann,22}^{\rm S/P} & 0\\ 0 & 0 & K_{\rm ann,33}^{\rm S/P} \end{bmatrix}.$$
 (4.24)

4.4.7 Step VI: Clear wood sample

Finally, the wood rays traversing the layered clear wood material have to be considered. This is done in another homogenization step formulated for an RVE of clear wood with about 5–10 mm characteristic length. Therein, elliptic cylindrical inclusions with main extension in radial direction and characteristic diameters of 50-500 µm, representing the ray cell material of homogenization step III(c), are embedded in a contiguous matrix built up by the layered material of homogenization step IV. The volume fractions occupied by these two phases are $f_{\rm ray}$ and $f_{\rm ann}$, $f_{\rm ray} + f_{\rm ann} = 1$. Using again a Mori-Tanaka scheme for the estimation of the thermal conductivity of the wood sample, $\mathbf{K}_{\rm wood}^{\rm MT}$, Eq. (4.1) is specified for one (elliptic cylindrical) inclusion phase as the wood rays, and the annual ring matrix, i.e. for $r, s \in$ [ray, ann], for $\mathbf{K}_{\rm ray}^{\rm MT}$ from Eq. (4.20), for $\mathbf{K}^0 = \mathbf{K}_{\rm ann}^{\rm S/P}$ from Eq. (4.24), and for $\mathbf{P}_{\rm ray}^0 = \mathbf{P}_{\rm ellcyl}^{\rm ann}$, resulting in

$$\mathbf{K}_{\text{wood}}^{\text{MT}} = \left\{ \hat{f}_{\text{ann}} \mathbf{K}_{\text{ann}}^{\text{S/P}} + \hat{f}_{\text{ray}} \mathbf{K}_{\text{ray}}^{\text{MT}} \cdot \left[\mathbf{I} + \mathbf{P}_{\text{ellcyl}}^{\text{ann}} \cdot \left(\mathbf{K}_{\text{ray}}^{\text{MT}} - \mathbf{K}_{\text{ann}}^{\text{S/P}} \right) \right]^{-1} \right\} \cdot \left\{ \hat{f}_{\text{ann}} \mathbf{I} + \hat{f}_{\text{ray}} \left[\mathbf{I} + \mathbf{P}_{\text{ellcyl}}^{\text{ann}} \cdot \left(\mathbf{K}_{\text{ray}}^{\text{MT}} - \mathbf{K}_{\text{ann}}^{\text{S/P}} \right) \right]^{-1} \right\}^{-1}.$$

$$(4.25)$$

The components of the **P**-tensor $\mathbf{P}_{\text{ellcyl}}^{\text{ann}}$ can be calculated from Eq. (4.2) with diameters derived subsequently in Subsection 4.5.2.

The cross-sectional dimensions of the rays are similar to those of the vessels and, thus, clearly below the characteristic widths of the growth rings considered in homogenization step V. Still homogenization step VI does not mean an interference with the principle of separation of scales invoked in Section 4.2, since the decisive dimensions of the two steps are different (R for step V, L and T for step VI), and therefore the steps don't affect each other. Actually, they are exchangeable without effect on the final result.

4.5 Composition and morphological properties of wood

4.5.1 Composition of different wood samples

Evaluation of the multiscale homogenization model requires determination of the volume fractions of the different phases of homogenization steps I to VI (Fig. 4.2). The volume fractions of steps I and II are determined as described in Hofstetter et al. [44]. The only difference to Hofstetter et al. [44] is the aggregation of the crystalline cellulose phase and the amorphous cellulose phase into one cellulose phase, with $f_{cel} = f_{crycel} + f_{amocel}$. The steps III, V, and VI are somewhat different to Hofstetter et al. [44]. The calculation of their associated volume fractions is presented in the following.

Volume fractions in earlywood, latewood, ray cell material (homogenization steps III(a), III(b), III(c))

The determination of the volume fractions of phases in earlywood emanates from the mass density of earlywood (including vessels). Kollmann [55] gives an according empirical equation for wood based on an average volumetric moisture expansion coefficient.

Approximately, this relation also applies to earlywood and latewood, therefore the dependence of the actual mass density on the dry density of earlywood $\rho_{\text{hard}+\text{ves}}^{\text{dry}}$ (see Eq. (4.30)) and the actual moisture content MC, respectively, can be approximated by:

$$\rho_{\text{hard}+\text{ves}}^{\text{wet}} = \rho_{\text{hard}+\text{ves}}^{\text{dry}} \frac{1 + MC}{1 + 0.84 \,\rho_{\text{hard}+\text{ves}}^{\text{dry}} MC}.$$
(4.26)

The mass density of the wet cell wall material, $\rho_{\rm cwm}^{\rm wet}$, is calculated according to Hofstetter et al. [44] as the weighted average of the mass densities of the chemical constituents (cellulose, hemicellulose, lignin, extractives) and of water, with the according volume fractions as weights. Knowledge of the mass densities $\rho_{\rm hard+ves}^{\rm wet}$ and $\rho_{\rm cwm}^{\rm wet}$ allows for computation of the total porosity (comprising lumens and vessels) in earlywood with empty pores, from

$$\hat{f}_{\rm por} = 1 - \frac{\rho_{\rm hard+ves}^{\rm wet}}{\rho_{\rm cwm}^{\rm wet}}.$$
(4.27)

Change of the reference volume from that of hardwood with vessels to that of earlywood without vessels results in

$$\hat{f}_{\text{lum}} = \frac{\hat{f}_{\text{por}} - \hat{f}_{\text{ves}}}{1 - \hat{f}_{\text{ves}}}.$$
 (4.28)

In softwoods, no vessels exist $(\hat{f}_{ves} = 0)$, so that Eq. (4.28) reduces to $\hat{f}_{lum} = \hat{f}_{por}$.

The volume fractions in latewood follow from substitution of 'hard+ves' by 'late', and of ' \hat{f}_r ' by ' \check{f}_r ', $r \in [\text{cwm, lum}]$, in Eqs. (4.26)-(4.28). For the ray cells, the according substitutions are 'hard+ves' by 'ray', and ' \hat{f}_r ' by ' \dot{f}_r ', $r \in [\text{cwm, lum}]$, in Eqs. (4.26)-(4.28). In both cases – latewood and ray tissue – the vessel volume fraction is zero ($\check{f}_{ves} = \dot{f}_{ves} = 0$). The density of the wood rays is set equal to the mean density of the whole wood sample, $\rho_{ray}^{dry} = \rho_{wood}^{dry}$.

Volume fractions in annual rings (homogenization step V)

The actually continuous density distribution across an annual ring is approximated by two sections with constant densities: the earlywood and the latewood sections with average mass densities of $\rho_{\text{hard}+\text{ves}}$ and ρ_{late} , respectively. The volume fractions within the annual rings, i.e. that of earlywood $\ddot{f}_{\text{hard}+\text{ves}}$ and that of latewood \ddot{f}_{late} [Fig. 4.2(V), Eq. (4.24)], are calculated following Kollmann [55]. For a sample with known wood species and given mean density $\rho_{\text{wood}}^{\text{dry}}$ in the dry state, at first the volume fraction of latewood, \ddot{f}_{late} , is calculated by use of species-dependent correlations between dry wood densities $\rho_{\text{wood}}^{\text{dry}}$ and latewood contents (stated in Table 4.2). Thereon, the volume fraction of hardwood with vessels, $\ddot{f}_{\text{hard}+\text{ves}}$, is obtained as

$$f_{\text{hard}+\text{ves}} = 1 - f_{\text{late}}.$$
(4.29)

Finally, by use of again species-dependent density ratios $(\rho_{\text{late}}/\rho_{\text{hard+ves}})_{\text{dry}}$ (see Table 4.2), the densities of dry hardwood with vessels and latewood, $\rho_{\text{hard+ves}}^{\text{dry}}$ and $\rho_{\text{late}}^{\text{dry}}$, follow from:

$$\rho_{\text{hard}+\text{ves}}^{\text{dry}} = \frac{\rho_{\text{wood}}^{\text{dry}}}{\ddot{f}_{\text{hard}+\text{ves}} + \ddot{f}_{\text{late}} \left(\frac{\rho_{\text{late}}}{\rho_{\text{hard}+\text{ves}}}\right)_{\text{dry}}},$$
(4.30)

$$\rho_{\text{late}}^{\text{dry}} = \rho_{\text{hard}+\text{ves}}^{\text{dry}} \left(\frac{\rho_{\text{late}}}{\rho_{\text{hard}+\text{ves}}}\right)_{\text{dry}}.$$
(4.31)

Volume fractions in clear wood sample (homogenization step VI)

The volume fractions within a clear wood sample, i.e. that of wood rays f_{ray} and that of annual ring material, $f_{ann} = 1 - f_{ray}$ (Fig. 4.2(VI), Eq. (4.25)), are determined based on literature data [110] for f_{ray} depending on the wood species (cf. Table 4.2).

Species	$\hat{f}_{\rm ves}$	$\acute{f}_{ m ray}$	$\left(\frac{a_2}{a_3}\right)_{\rm ray}$	$\left(\frac{\rho_{\rm late}}{\rho_{\rm hard+ves}}\right)_{\rm dry}$	$\ddot{f}_{ m late}$
Softwood					
Cedar	-	0.096	16/200	2.60	$0.857 \rho_{\rm wood}^{\rm dry} - 0.234$
Douglas fir	-	0.070	12/80	2.80	$1.161 \ \rho_{\rm wood}^{\rm dry} - 0.268$
Fir	-	0.096	16/200	2.30	$3.478 \ \rho_{\rm wood}^{\rm dry} - 1.009$
Hemlock	-	0.088	17/245	2.60	$3.750 \ \rho_{\rm wood}^{\rm dry} - 1.270$
Larch	-	0.088	16/190	2.40	$0.857 \ \rho_{\rm wood}^{\rm dry} - 0.234$
Pine	-	0.055	25/285	2.60	$1.161 \ \rho_{\rm wood}^{\rm dry} - 0.268$
Spruce	-	0.047	11/150	2.60	$3.750 \ \rho_{\rm wood}^{\rm dry} - 1.270$
Hardwood					
Ash	0.12	0.149	27/290	1.30	$1.846 \ \rho_{\rm wood}^{\rm dry} - 0.577$
Balsa	0.04	0.180	95/1850	1.10	0.20
Beech	0.25	0.157	60/1000	1.86	$2.313 \rho_{\rm wood}^{\rm dry} - 1.163$
Birch	0.25	0.105	15/240	1.10	0.25
Hickory	0.29	0.200	20/130	1.30	$1.846 \ \rho_{\rm wood}^{\rm dry} - 0.577$
Maple	0.07	0.172	25/270	1.50	$4.000 \ \rho_{\rm wood}^{\rm dry} - 2.000$
Oak	0.24	0.228	50/600	2.81	$1.678 \ \rho_{\rm wood}^{\rm dry} - 0.552$
Poplar	0.11	0.120	13/250	1.68	$4.061 \ \rho_{\rm wood}^{\rm dry} - 1.299$
Source	[44]	[110]	[110]	[110]	[55]

Table 4.2: Input data set II: Composition and morphology of different wood species

4.5.2 Morphological properties of different wood samples

Evaluation of the multiscale homogenization model also requires input of morphological properties of the inclusions making up the different phases in the homogenization steps I to VI (Fig. 4.2). In step I (polymer network) spherical inclusions are assumed, in steps II and IV (cell wall material, hardwood with vessels) circular cylindrical inclusions. The second order **P**-tensor used to describe these morphologies can be calculated directly from Eqs. (4.16) and (4.18) without specification of further morphological characteristics.

For steps III(a), III(b), III(c), and VI, dimensions of the involved inclusions of ellipsoidal and elliptic cylindrical shape are detailed next.

Dimensions of lumens in earlywood and latewood (homogenization steps III(a) and III(b))

Calculation of the second order **P**-tensor for ellipsoidal inclusions requires specification of the three principal radii of the ellipsoids (more precisely their ratios relative to one another). Depending on the local density of wood, the thickness of the cell walls and the dimensions of the tracheids change, especially in radial direction. The tangential cell diameter shows a much smaller variation and is set constant as $\hat{a}_{\rm T} = 50 \,\mu{\rm m}$. The length of the tracheids (in longitudinal direction) is taken as $\hat{a}_{\rm L} = 1.50 \,\mu{\rm m}$ [77]. The radial cell diameter, the cell wall thickness, and the thus following dimensions of the lumens are determined by empirical relations depending on local dry density proposed by Perré [77]. These relations are actually based on a rectangular representation of the cross-sections of the tracheids, but are used here as reasonable approximations as well. Starting with earlywood, the radial dimension of the wood cell reads as

$$\hat{a}_{\rm R} = 5.75 \times 10^{-5} - 3.75 \times 10^{-5} \,\rho_{\rm early}^{\rm dry} \,[{\rm g/cm}^3] \qquad [{\rm m}] \,.$$

$$(4.32)$$

Based on the radial and tangential dimensions, $\hat{a}_{\rm R}$ and $\hat{a}_{\rm T}$, and the volume fraction of the cell wall, \hat{f}_{cwm} , the cell wall thickness can be calculated as

$$\hat{t} = \frac{1}{4}\,\hat{a}_{\rm R} + \frac{1}{4}\,\hat{a}_{\rm T} - \frac{1}{4}\,\sqrt{\hat{a}_{\rm R}^2 + 2\,\hat{a}_{\rm R}\,\hat{a}_{\rm T} + \hat{a}_{\rm T}^2 - 4\,\hat{f}_{cwm}\,\hat{a}_{\rm R}\,\hat{a}_{\rm T}}.$$
(4.33)

Unlike the model of Perré [77], moisture-dependent changes of the cell wall thickness are taken into account through considering the cell wall fraction $\hat{f}_{\rm cwm}$ in the wet state. In a simplified manner, the ratio of radial and tangential cell dimensions is held constant during changes of the moisture content, meaning that isotropy of dimensional changes in the transverse plane is assumed.

In the multiscale model, the lumens are considered as ellipsoidal inclusions, having diameters equal to the dimensions of the cuboid-shaped inclusions described afore. The aspect ratios of their diameters are determined from the three dimensions of the lumens, $\hat{a}_{\rm R}$, $\hat{a}_{\rm T}$, and $\hat{a}_{\rm L}$, and the cell wall thickness \hat{t} :

$$\frac{\hat{a}_1}{\hat{a}_3} = \frac{\hat{a}_{\rm R} - 2\,\hat{t}}{\hat{a}_{\rm L}}, \qquad \frac{\hat{a}_2}{\hat{a}_3} = \frac{\hat{a}_{\rm T} - 2\,\hat{t}}{\hat{a}_{\rm L}}.$$
(4.34)

For a shorter calculation time of the micromechanical model, the longitudinal dimension \hat{a}_L is assumed to be infinite for the case of thermal conduction. This is physically permissible, since the cell walls act as mean heat transport routes, and the lumens only contribute a minor share, because of the much lower thermal conductivity of the lumens compared to the cell walls.

The corresponding ellipsoidal dimensions of the lumens in latewood, \check{a}_1 , \check{a}_2 , and \check{a}_3 , follow from substitution of "hard+ves" by "late", and of " \hat{f}_{cwm} " by " \check{f}_{cwm} " in Eqs. (4.32)-(4.34). Again, the ellipsoids are replaced by cylinders in practical applications in order to reduce calculation time.

Dimensions of lumens in the ray cell material (homogenization step III(c))

The shape of the cells building up the wood rays is reproduced by ellipsoidal inclusions with circular cross-sections. Based on pictures of sections through ray cell bundles in Wagenführ [110], the ratios of the three principal ellipsoidal radii are chosen as:

$$\frac{\dot{a}_1}{\dot{a}_3} = 4, \qquad \frac{\dot{a}_2}{\dot{a}_3} = 1.$$
 (4.35)

For the case of thermal conductivity, $\frac{\dot{a}_1}{\dot{a}_3}$ is assumed to be infinite. As described before in relation to the longitudinal extension of the lumen, this reduces calculation time while being physically admissible due to the predominance of the heat transport routes through the cell walls.

Dimension of wood rays (homogenization step VI)

Wood rays are represented by ellipsoidal cylinders in the model which run throughout the wood tissue in the radial direction. Based on typical dimensions of wood rays specified by Wagenführ [110], average ratios of tangential and longitudinal radii of ray cells, $(a_2/a_3)_{ray}$, of different wood species can be calculated. They are summarized in Table 4.2. The ratios of the three radii, which are required for the calculation of the **P**-tensor of the ray cells, are therefore:

$$\frac{\dot{a}_1}{\dot{a}_3} = \infty, \qquad \frac{\dot{a}_2}{\dot{a}_3} = \left(\frac{a_2}{a_3}\right)_{\rm ray}.$$
(4.36)

4.6 Experimental validation

4.6.1 Strategy

The validation of the multiscale model for thermal conductivity is based on experimental data from literature. Model predictions, i.e. conductivity values $\mathbf{K}_{\text{wood}}^{\text{MT}}$, are computed on the basis of tissue-independent phase conductivities λ_{hemcel} , λ_{lig} , $\lambda_{\text{H}_2\text{Oext}}$, \mathbf{K}_{cel} , and λ_{air} (input data set I, Table 4.1) and given sample-specific volume fractions and morphological properties (input data set II, Table 4.2). These model predictions are compared with corresponding experimentally determined thermal conductivities of macroscopic (clear) wood samples (experimental data set, Section 4.6.2).

4.6.2 Tissue-dependent thermal properties of different wood samples

The thermal conductivities of different wood samples are usually determined by means of a steady-state hot-plate method. A review of test data for wood is given by Ratcliffe [80, 81, 82]. Evaluation of the presented multiscale model requires knowledge of

- species,
- oven-dry density,

- moisture content,
- temperature,
- the direction of heat flux.

Only test results where all of these data are specified are considered in the model validation, namely results reported by Griffiths [32], Rowley [86], Wangaard [111], Narayanamurti [71]), and MacLean [63]. In Maku [64], Ražnjević [83], and Grønli [34], unfortunately the moisture content is not reported, so that the respective data sets cannot be used. In the end, 452 complete data sets of 48 different European and American wood species (see Table 4.4 in the appendix of this chapter) could be collected.

All data sets confirm the orthotropy of the thermal conductivity of wood with principal material directions along the stem axis (longitudinal direction L), normal to the growth rings (radial direction R), and tangential to them (tangential direction T), see Fig. 2.1(a). The difference between axial and transverse properties, e.g. between thermal conductivities $\lambda_{\rm L}$ and $\lambda_{\rm R}$, is by far larger than that between radial and tangential properties, e.g. between $\lambda_{\rm R}$ and $\lambda_{\rm T}$. Some of the sources specify values for the "radial–oblique", the "transversal/oblique", and the "tangential–oblique" directions, which denote measuring directions not coinciding with the principal material directions of wood. For comparison, the thermal conductivity was evaluated at inclination angles of 22.5°, 45.0° or 67.5°, respectively, towards the radial direction in the cross-sectional plane in these cases.

4.6.3 Comparison between model estimates and experimental thermal conductivity values

The experimental validation of the developed multiscale model is done by a comparison of model predictions for thermal conductivities, computed from Eq. (4.25), for given sample-specific volume fractions and morphological properties, with corresponding experimental measurement results. The comparison is illustrated in Fig. 4.3, where each marker indicates one pair of thermal conductivity measurement and corresponding model prediction. Different markers are used for softwood and hardwood species and for the three principal material directions L, R, and T. Measurements in the transverse plane inclined to the principal directions R and T are referred to as "trans" without further differentiation. The solid diagonal line indicates perfect agreement between model predicted and experimental values.

In order to quantify the agreement, differences between predicted estimates and experimental measurements are determined in terms of mean values and standard deviations of relative prediction errors, \bar{e} and s. Beside these error measures, the correlation coefficients r^2 are determined.

The model estimates for the transversal thermal conductivity (i.e. radial, tangential, and transversal values), λ_{trans} , show a good agreement with the measured values. The correlation coefficient is $r^2 = 90.7 \%$, the error measures amount to $\bar{e} = -11.5 \%$ and s = 9.1 %. Obviously, the model tends to slightly underestimate the transversal conductivity of macroscopic wood. The quality of correlation slightly depends on the source of the values, which might be due to different measurement methods.



Figure 4.3: Comparison of predicted and measured thermal conductivities

As compared to the mean values of the errors between model predictions and experimental results, the corresponding standard deviations are relatively low and can be explained by variations within the species – in the model average values for each species are used – and, eventually, by limited accuracy of the underlying experimental results. The general tendency to underestimation might be caused by inaccurate and insecure input values for the thermal conductivities of the cell wall constituents, which partly had to be estimated for lack of suitable direct measurement results.

For the longitudinal thermal conductivity $\lambda_{\rm L}$ only eight data sets are available from only one literature source [32]. Thus the correlation coefficient of $r^2 = 41.2 \%$ has only a limited significance. The error measures of $\bar{e} = +2.8 \%$ and s = 4.4 % show a slight overestimation of the longitudinal thermal conductivity by the model. A similar tendency to overestimation was also observed for the transversal data from the same source. On the whole, the prediction quality of the model for longitudinal thermal conductivity appears reasonable.

4.7 Macroscopic regression functions based on the multiscale model

The model presented in this chapter allows for predictions of thermal conductivities for many different, also non-tested configurations. Due to its analytical formulation this takes only a few seconds. However, in practical use (e.g. in a finite element calculation) a regression function is more convenient. For this purpose, the predictions of the multiscale model for a specific wood species were fitted by an appropriate polynomial, considering dependence on density, temperature, and moisture content. The polynomial reads as

$$\lambda_{i} = \lambda_{i}^{\text{ref}} \left(a_{10,i} + a_{11,i} \overline{\rho} + a_{12,i} \overline{\rho}^{2} + a_{13,i} \overline{\rho}^{3} \right) \left(a_{20,i} + a_{21,i} \overline{T} + a_{22,i} \overline{T}^{2} \right) \left(a_{30,i} + a_{31,i} \overline{MC} + a_{32,i} \overline{MC}^{2} \right) \quad [W/(m \, \text{K})], \quad i \in [\text{R}, \text{ T}, \text{ L}]$$
(4.37)

where $\overline{\rho}$, \overline{T} , and \overline{MC} are density, temperature, and moisture content related to reference conditions:

$$\overline{\rho} = \frac{\rho_{\text{wood}}^{\text{dry}}}{450 \,\text{kg/m}^3}, \quad \overline{T} = \frac{T}{293.15 \,\text{K}}, \quad \overline{MC} = \frac{MC}{12 \,\%}.$$
(4.38)

 λ_i^{ref} is the thermal conductivity in direction i = R, T, L at reference conditions. The fitting coefficients *a* for spruce are given in Table 4.3. They are valid for a density $\rho_{\text{wood}}^{\text{dry}}$ from 300 to 750 kg/m³, a moisture content *MC* from 0.05 to 0.25, and a temperature *T* from 273.15 to 353.15 K (0–80 °C).

Table 4.3: Reference values $\lambda_i^{\text{ref}} [W/(m \text{ K})]$ and coefficients a_i for directions i = R, T, L, used in Eq. (4.37) for spruce clear wood, calculated based on results of the multiscale homogenization model.

i	R (radial)	T (tangential)	L (longitudinal)
$\lambda_i^{\rm ref}$	0.08952	0.10571	0.22230
$a_{10,i}$	-0.28394	-0.37026	0.23787
$a_{11,i}$	3.38383	1.96078	0.52149
$a_{12,i}$	-3.69203	-0.89819	0.20161
$a_{13,i}$	1.51439	0.21972	-0.04841
$a_{20,i}$	0.36715	0.39537	0.59275
$a_{21,i}$	0.75548	0.73931	0.48164
$a_{22,i}$	-0.20293	-0.22270	-0.16189
$a_{30,i}$	0.82074	0.80087	0.85721
$a_{31,i}$	0.08485	0.09854	0.04871
$a_{32,i}$	0.04990	0.05198	0.02636

4.8 Summary

In this chapter, the basic model for multiscale modeling of transport processes is developed and evaluated for thermal conductivity. The obtained results demonstrate the considerably good predictive capabilities of the application of mean-field homogenization techniques to the hierarchically structured material wood, as it was already shown by an existing micromechanical model for the material's elastic behavior [44]. In contrast to currently available models for estimation of thermal transport properties, the presented model starts at a tissue-independent level and allows to calculate the overall behavior of a macroscopic wood sample only based on its microstructure and physical properties of elementary constituents at the microscale. Average thermal conductivities of the dry cell wall (back-calculated from macroscopic measurements) are not needed in the presented model. In the following chapter, the model will be adapted for diffusion.

4.9 Appendix: Thermal conductivity measurements

No.	Species	Direction	MC	T	$\rho_{\rm wood}^{\rm dry}$	$\lambda^{ ext{exp}}$	
	(as reported)		[1]	[K]	$\left[\text{g/cm}^3\right]$	[W/(mK)]	
1	Ash	Т	0.155	293.15	0.740	0.153	[32]
2	Ash	Т	0.155	298.15	0.740	0.160	[32]
3	Ash	R	0.150	293.15	0.740	0.155	[32]
4	Ash	R	0.150	298.15	0.740	0.155	[32]
5	Ash	L	0.143	293.15	0.740	0.299	[32]
6	Ash	L	0.143	298.15	0.740	0.304	[32]
7	Ash	Т	0.160	293.15	0.740	0.194	[32]
8	Ash	Т	0.160	298.15	0.740	0.196	[32]
9	Ash	R	0.166	293.15	0.740	0.174	[32]
10	Ash	R	0.166	298.15	0.740	0.176	[32]
11	Ash	L	0.149	293.15	0.740	0.316	[32]
12	Ash	L	0.149	298.15	0.740	0.323	[32]
13	Spruce	Т	0.152	298.15	0.700	0.164	[32]
14	Spruce	Т	0.152	299.15	0.700	0.167	[32]
15	Spruce	R	0.152	300.15	0.700	0.147	[32]
16	Spruce	R	0.152	301.15	0.700	0.148	[32]
17	Spruce	L	0.145	302.15	0.700	0.294	[32]
18	Spruce	L	0.145	303.15	0.700	0.300	[32]
19	Spruce	Т	0.149	304.15	0.700	0.174	[32]
20	Spruce	Т	0.149	305.15	0.700	0.175	[32]
21	Spruce	R	0.127	306.15	0.700	0.162	[32]
22	Spruce	R	0.127	307.15	0.700	0.164	[32]
23	Spruce	L	0.152	308.15	0.700	0.325	[32]
24	Spruce	L	0.152	309.15	0.700	0.331	[32]
25	Oak	R	0.137	293.15	0.600	0.117	[32]
26	Cedar	R	0.134	293.15	0.490	0.121	[32]
27	Cedar	R	0.127	293.15	0.480	0.106	[32]
28	Cedar	R	0.106	293.15	0.480	0.116	[32]
29	Balsa	R	0.130	293.15	0.100	0.046	[32]
30	Fir	trans	0.150	293.15	0.600	0.117	[32]
31	Pinus excelsa	R	0.110	293.55	0.480	0.108	[71]
32	Cedrus deodara	R	0.070	294.15	0.542	0.131	71
33	Picea morinda	Т	0.140	294.09	0.571	0.120	[71]

Table 4.4: Experimental data set: Thermal conductivities of wood samples, with corresponding density, moisture content and temperature

No	Species	Direction			dry	\ exp	
110.	(as reported)	Direction	[1]	1 [K]	$\rho_{\rm wood}$	\sqrt{M}	
			[1]				[= 1]
34	Quercus	Т	0.124	292.81	0.897	0.190	[71]
35	Aspen, bigtooth	trans	0.000	302.59	0.410	0.102	[63]
36	Balsa	trans	0.000	302.59	0.160	0.059	[63]
37	Douglas-fir	trans	0.000	302.59	0.460	0.110	[63]
38	Fir, white	trans	0.000	302.59	0.410	0.102	[63]
39	Hemlock, western	trans	0.000	302.59	0.460	0.114	[63]
40	Larch, western	trans	0.000	302.59	0.570	0.136	[63]
41	Maple, sugar	trans	0.000	302.59	0.680	0.163	[63]
42	Oak, red	trans	0.000	302.59	0.670	0.172	[63]
43	Pine, southern yellow	trans	0.000	302.59	0.560	0.136	[63]
44	Pine, white	trans	0.000	302.59	0.400	0.104	[63]
45	Redcedar, western	trans	0.000	302.59	0.340	0.092	[63]
46	Spruce, Engelmann	trans	0.000	302.59	0.340	0.089	[63]
47	Pine, white	trans	0.000	302.59	0.400	0.104	[63]
48	Ash, white	trans	0.156	302.59	0.560	0.175	[63]
49	Aspen, bigtooth	trans	0.121	302.59	0.410	0.118	[63]
50	Balsa	trans	0.080	302.59	0.170	0.068	[63]
51	Birch, yellow	trans	0.108	302.59	0.640	0.172	[63]
52	Douglas-fir	trans	0.184	302.59	0.460	0.140	[63]
53	Larch, western	trans	0.126	302.59	0.460	0.140	[63]
54	Maple, sugar	trans	0.117	302.59	0.660	0.202	[63]
55	Oak, red	trans	0.124	302.59	0.620	0.195	[63]
56	Oak, white	trans	0.111	302.59	0.620	0.198	[63]
57	Pine, southern yellow	trans	0.138	302.59	0.530	0.162	[63]
58	Pine, white	trans	0.098	302.59	0.360	0.111	[63]
59	Redcedar, western	trans	0.133	302.59	0.320	0.100	[63]
60	Spruce, Engelmann	trans	0.130	302.59	0.350	0.110	[63]
61	Beech, American	trans	0.111	302.59	0.590	0.169	[63]
62	Fir, white	trans	0.117	302.59	0.380	0.113	[63]
63	Maple, silver	trans	0.099	302.59	0.470	0.154	[63]
64	Sycamore, American	trans	0.090	302.59	0.520	0.154	[63]
65	Ponderosa Pine	trans	0.019	297.04	0.375	0.096	[86]
66	Ponderosa Pine	trans	0.035	297.04	0.373	0.098	[86]
67	Ponderosa Pine	trans	0.075	297.04	0.368	0.103	[86]
68	Ponderosa Pine	trans	0.087	297.04	0.366	0.104	[86]
69	Ponderosa Pine	trans	0.158	297.04	0.352	0.112	[86]
70	Ponderosa Pine	trans	0.227	297.04	0.343	0.121	[86]
71	Ponderosa Pine	trans	0.036	297.04	0.489	0.114	[86]
72	Ponderosa Pine	trans	0.044	297.04	0.487	0.115	[86]
73	Ponderosa Pine	trans	0.072	297.04	0.480	0.118	[86]
74	Ponderosa Pine	trans	0.113	297.04	0.470	0.124	[86]
75	Ponderosa Pine	trans	0.155	297.04	0.460	0.130	[86]
					Contin	ued on next	page

Table 4.4 – continued from previous page

	Table 4.4 – continued from previous page								
No.	Species	Direction	MC	T	$\rho_{\rm wood}^{\rm dry}$	$\lambda^{ ext{exp}}$			
	(as reported)		[1]	[K]	$\left[\mathrm{g/cm}^3\right]$	[W/(mK)]			
76	Ponderosa Pine	trans	0.189	297.04	0 454	0.136	[86]		
77	Ponderosa Pine	trans	0.020	297.04	0.391	0.105	[86]		
78	Ponderosa Pine	trans	0.067	297.04	0.387	0.114	[86]		
79	Ponderosa Pine	trans	0.070	297.04	0.385	0.113	[86]		
80	Ponderosa Pine	trans	0.194	297.04	0.371	0.134	[86]		
81	Ponderosa Pine	trans	0.237	297.04	0.366	0.142	[86]		
82	Ponderosa Pine	trans	0.297	297.04	0.365	0.153	[86]		
83	Ponderosa Pine	trans	0.126	297.04	0.421	0.125	[86]		
84	Ponderosa Pine	trans	0.137	297.04	0.414	0.124	[86]		
85	Ponderosa Pine	trans	0.139	297.04	0.418	0.123	[86]		
86	Ponderosa Pine	trans	0.225	297.04	0.407	0.142	[86]		
87	Ponderosa Pine	trans	0.299	297.04	0.402	0.156	[86]		
88	Shortleaf Yellow Pine	trans	0.001	297.04	0.585	0.124	[86]		
89	Shortleaf Yellow Pine	trans	0.039	297.04	0.573	0.131	[86]		
90	Shortleaf Yellow Pine	trans	0.101	297.04	0.554	0.140	[86]		
91	Shortleaf Yellow Pine	trans	0.135	297.04	0.544	0.144	[86]		
92	Shortleaf Yellow Pine	trans	0.005	297.04	0.526	0.128	[86]		
93	Shortleaf Yellow Pine	trans	0.031	297.04	0.521	0.131	[86]		
94	Shortleaf Yellow Pine	trans	0.055	297.04	0.518	0.136	[86]		
95	Shortleaf Yellow Pine	trans	0.070	297.04	0.509	0.141	[86]		
96	Shortleaf Yellow Pine	trans	0.123	297.04	0.498	0.147	[86]		
97	Shortleaf Yellow Pine	trans	0.139	297.04	0.494	0.147	[86]		
98	Shortleaf Yellow Pine	trans	0.012	297.04	0.482	0.111	[86]		
99	Shortleaf Yellow Pine	trans	0.067	297.04	0.476	0.123	[86]		
100	Shortleaf Yellow Pine	trans	0.069	297.04	0.476	0.123	[86]		
101	Shortleaf Yellow Pine	trans	0.293	297.04	0.442	0.166	[86]		
102	Shortleaf Yellow Pine	trans	0.002	297.04	0.489	0.119	[86]		
103	Shortleaf Yellow Pine	trans	0.033	297.04	0.485	0.122	[86]		
104	Shortleaf Yellow Pine	trans	0.068	297.04	0.481	0.127	[86]		
105	Shortleaf Yellow Pine	trans	0.120	297.04	0.455	0.134	[86]		
106	Shortleaf Yellow Pine	trans	0.169	297.04	0.447	0.139	[86]		
107	Shortleaf Yellow Pine	trans	0.178	297.04	0.448	0.141	[86]		
108	Shortleaf Yellow Pine	trans	0.192	297.04	0.441	0.143	[86]		
109	Shortleaf Yellow Pine	trans	0.229	297.04	0.434	0.144	[86]		
110	White Oak	trans	0.051	297.04	0.749	0.173	[86]		
111	White Oak	trans	0.072	297.04	0.737	0.176	[86]		
112	White Oak	trans	0.087	297.04	0.727	0.178	[86]		
113	White Oak	trans	0.106	297.04	0.721	0.181	[86]		
114 115	white Oak White Oal-	trans	0.005	297.04	0.600	0.150	[80] [86]		
110		trans	0.074	297.04	0.590	0.107	[00]		
116	White Oak	trans	0.094	297.04	0.585	0.160	[86]		
117	White Oak	trans	0.114	297.04	0.577	0.162	[86]		

No	Species	Direction	MC	T	o ^{dry} .	$\lambda^{ m exp}$	
1.0.	(as reported)	Direction	[1]	[K]	$\left[g/cm^{3} \right]$	[W/(mK)]	
118	Red Oak	trans	0.048	297.04	0 731	0.170	[86]
119	Red Oak	trans	0.040 0.055	297.04 297.04	0.731 0.733	0.170 0.173	[86]
120	Red Oak	trans	0.061	297.04	0.735	0.177	[86]
121	Red Oak	trans	0.077	297 04	0 723	0.176	[86]
122	Red Oak	trans	0.088	297.04 297.04	0.714	0.178	[86]
123	Red Oak	trans	0.101	297.04	0.706	0.179	[86]
124	Red Oak	trans	0.055	297.04	0.658	0.162	[86]
125	Red Oak	trans	0.055	297.04	0.667	0.164	[86]
126	Red Oak	trans	0.060	297.04	0.665	0.163	[86]
127	Red Oak	trans	0.068	297.04	0.660	0.164	[86]
128	Red Oak	trans	0.091	297.04	0.646	0.167	[86]
129	Red Oak	trans	0.119	297.04	0.633	0.169	[86]
130	Yellow Birch	trans	0.057	297.04	0.598	0.138	[86]
131	Yellow Birch	trans	0.078	297.04	0.590	0.140	[86]
132	Yellow Birch	trans	0.093	297.04	0.584	0.142	[86]
133	Yellow Birch	trans	0.157	297.04	0.559	0.150	[86]
134	Yellow Birch	trans	0.056	297.04	0.560	0.126	[86]
135	Yellow Birch	trans	0.098	297.04	0.550	0.134	[86]
136	Yellow Birch	trans	0.118	297.04	0.543	0.136	[86]
137	Yellow Birch	trans	0.169	297.04	0.526	0.141	[86]
138	Yellow Birch	trans	0.035	297.04	0.620	0.123	[86]
139	Yellow Birch	trans	0.060	297.04	0.617	0.128	[86]
140	Yellow Birch	trans	0.155	297.04	0.582	0.139	[86]
141	Yellow Birch	trans	0.166	297.04	0.578	0.140	[86]
142	Yellow Birch	trans	0.017	297.04	0.709	0.139	[86]
143	Yellow Birch	trans	0.041	297.04	0.697	0.148	[86]
144	Yellow Birch	trans	0.066	297.04	0.691	0.149	[86]
145	Yellow Birch	trans	0.120	297.04	0.652	0.166	[86]
146	Yellow Birch	trans	0.138	297.04	0.648	0.166	[86]
147	Yellow Birch	trans	0.151	297.04	0.642	0.170	[86]
148	Yellow Birch	trans	0.228	297.04	0.618	0.177	[86]
149	Yellow Birch	trans	0.253	297.04	0.606	0.173	[86]
150	Douglas Fir	trans	0.108	297.04	0.458	0.106	[86]
151	Douglas Fir	trans	0.108	297.04	0.453	0.109	[86]
152	Douglas Fir	trans	0.108	297.04	0.509	0.112	[86]
153	Douglas Fir	trans	0.101	297.04	0.479	0.110	[86]
154	Douglas Fir	trans	0.105	297.04	0.449	0.104	[86]
155	Douglas Fir	trans	0.103	297.04	0.494	0.110	[86]
156	Douglas Fir	trans	0.109	297.04	0.521	0.114	[86]
157	Douglas Fir	trans	0.109	297.04	0.489	0.110	[86]
158	Douglas Fir	trans	0.109	297.04	0.470	0.106	[86]
159	Douglas Fir	trans	0.056	297.04	0.443	0.099	[86]

Table 4.4 – continued from previous page

	Table 4	$4.4 - \operatorname{continu}$	ied fron	ı previou	s page		
No.	Species	Direction	MC	T	$\rho_{\rm max}^{\rm dry}$	$\lambda^{ ext{exp}}$	
	(as reported)		[1]	[K]	$\left[g/cm^{3} \right]$	[W/(mK)]	
160	Douglas Fir	trans	0.059	297.04	0.482	0.103	[86]
161	Douglas Fir	trans	0.056	297.04	0.526	0.108	[86]
162	Douglas Fir	trans	0.065	297.04	0.422	0.102	[86]
163	Hard Maple	trans	0.056	297.04	0.637	0.156	[86]
164	Hard Maple	trans	0.061	297.04	0.712	0.160	[86]
165	Hard Maple	trans	0.061	297.04	0.705	0.165	[86]
166	Hard Maple	trans	0.061	297.04	0.666	0.161	[86]
167	Hard Maple	trans	0.060	297.04	0.641	0.160	[86]
168	Hard Maple	trans	0.066	297.04	0.619	0.159	[86]
169	Hard Maple	trans	0.059	297.04	0.627	0.151	[86]
170	Hard Maple	trans	0.060	297.04	0.648	0.155	[86]
171	Longleaf Yellow Pine	trans	0.066	297.04	0.648	0.144	[86]
172	Longleaf Yellow Pine	trans	0.077	297.04	0.611	0.135	[86]
173	Longleaf Yellow Pine	trans	0.071	297.04	0.597	0.133	[86]
174	Longleaf Yellow Pine	trans	0.066	297.04	0.535	0.128	[86]
175	Longleaf Yellow Pine	trans	0.067	297.04	0.518	0.120	[86]
176	Longleaf Yellow Pine	trans	0.631	297.04	0.320	0.118	[86]
177	Longleaf Yellow Pine	trans	0.074	297.04	0.459	0.123	[86]
178	Longleaf Yellow Pine	trans	0.075	297.04	0.455	0.125	[86]
179	Norway Pine	trans	0.068	297.04	0.498	0.119	[86]
180	Norway Pine	trans	0.064	297.04	0.487	0.116	[86]
181	Norway Pine	trans	0.071	297.04	0.479	0.122	[86]
182	Norway Pine	trans	0.059	297.04	0.478	0.118	[86]
183	Norway Pine	trans	0.065	297.04	0.463	0.117	[86]
184	Norway Pine	trans	0.062	297.04	0.458	0.109	[86]
185	Norway Pine	trans	0.064	297.04	0.415	0.104	[86]
186	Norway Pine	trans	0.064	297.04	0.390	0.104	[86]
187	Norway Pine	trans	0.061	297.04	0.369	0.107	[86]
188	Ponderosa Pine	trans	0.083	297.04	0.513	0.126	[86]
189	Ponderosa Pine	trans	0.089	297.04	0.482	0.120	[86]
190	Ponderosa Pine	trans	0.082	297.04	0.464	0.115	[86]
191	Ponderosa Pine	trans	0.063	297.04	0.443	0.108	[86]
192	Ponderosa Pine	trans	0.081	297.04	0.409	0.112	[86]
193	Ponderosa Pine	trans	0.086	297.04	0.389	0.107	[86]
194	Ponderosa Pine	trans	0.091	297.04	0.387	0.107	[86]
195	Red Oak	trans	0.054	297.04	0.754	0.185	[86]
196	Red Oak	trans	0.071	297.04	0.642	0.165	[86]
197	Red Oak	trans	0.067	297.04	0.643	0.158	[86]
198	Red Oak	trans	0.056	297.04	0.626	0.155	[86]
199	Red Oak	trans	0.058	297.04	0.598	0.151	[86]
200	Red Oak	trans	0.059	297.04	0.582	0.150	[86]
201	Shortleaf Yellow Pine	trans	0.072	297.04	0.603	0.157	[86]

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 $Continued \ on \ next \ page$

No	Species	Direction	MC	T	odry	$\lambda \exp$	
110.	(as reported)	Direction	[1]	[K]	$\left[\text{g/cm}^3 \right]$	[W/(mK)]	
202	Shortloof Vollow Pino	trong	0.061	207.04	0 501	0.140	[86]
202	Shortleaf Vellow Pine	trans	0.001 0.067	297.04 297.04	0.591 0.455	0.140 0.127	[86]
$200 \\ 204$	Shortleaf Yellow Pine	trans	0.001	297.04 297.04	0.400 0.522	0.121	[86]
201 205	Shortleaf Yellow Pine	trans	0.059	297.04	0.388	0.115	[86]
206	Shortleaf Vellow Pine	trans	0.046	297.04	0.394	0.116	[86]
$200 \\ 207$	Shortleaf Vellow Pine	trans	0.040	297.04 297.04	0.395	0.113	[86]
201	Shortleaf Yellow Pine	trans	0.000	297.04 297.04	0.500 0.502	0.133	[86]
$200 \\ 209$	Shortleaf Yellow Pine	trans	0.068	297.04	0.468	0.123	[86]
$\frac{-00}{210}$	Sitka Spruce	trans	0.063	297.04	0.445	0.098	[86]
 911	Sitka Spruce	trans	0.063	297.04	0.424	0.091	[86]
$\frac{211}{919}$	Sitka Spruce	trans	0.000	297.04 297.04	0.424	0.091	[86]
212	Sitka Spruce	trans	0.004	297.04 297.04	0.490	0.090	[86]
210	Sitka Spruce	trans	0.060	297.01 297.04	0.390	0.091	[86]
215	Sitka Spruce	trans	0.064	297.04	0.385	0.092	[86]
216	Sitka Spruce	trans	0.066	297.04	0.347	0.084	[86]
217	Sitka Spruce	trans	0.069	297.04	0.329	0.089	[86]
218	Soft Maple	trans	0.060	297.04	0.590	0.139	[86]
219	Soft Maple	trans	0.065	297.04	0.546	0.141	[86]
220	Soft Maple	trans	0.061	297.04	0.571	0.135	[86]
221	Soft Maple	trans	0.060	297.04	0.571	0.137	[86]
222	Soft Maple	trans	0.063	297.04	0.587	0.144	[86]
223	Soft Maple	trans	0.061	297.04	0.625	0.143	[86]
224	Sugar Pine	trans	0.084	297.04	0.400	0.104	[86]
225	Sugar Pine	trans	0.084	297.04	0.386	0.094	[86]
226	Sugar Pine	trans	0.086	297.04	0.357	0.090	[86]
227	Sugar Pine	trans	0.083	297.04	0.355	0.093	[86]
228	Sugar Pine	trans	0.083	297.04	0.346	0.092	[86]
229	Sugar Pine	trans	0.089	297.04	0.340	0.091	[86]
230	Western Larch	trans	0.100	297.04	0.650	0.153	[86]
231	Western Larch	trans	0.097	297.04	0.612	0.153	[86]
232	Western Larch	trans	0.105	297.04	0.599	0.142	[86]
233	Western Larch	trans	0.103	297.04	0.576	0.142	[86]
234	Western Larch	trans	0.103	297.04	0.545	0.139	[86]
235	Western Larch	trans	0.108	297.04	0.476	0.128	[86]
236	Western Larch	trans	0.106	297.04	0.475	0.120	[86]
237	Western Red Cedar	trans	0.110	297.04	0.381	0.112	[86]
238	Western Red Cedar	trans	0.116	297.04	0.360	0.101	[86]
239	Western Red Cedar	trans	0.102	297.04	0.327	0.089	[86]
240	Western Red Cedar	trans	0.100	297.04	0.330	0.089	[86]
241	Western Red Cedar	trans	0.097	297.04	0.333	0.088	[86]
242	Western Red Cedar	trans	0.083	297.04	0.323	0.087	[86]
243	Western Red Cedar	trans	0.081	297.04	0.324	0.081	[86]

Table 4.4 – continued from previous page

	Table 4.4 – continued from previous page							
No.	Species	Direction	MC	T	$\rho_{\rm wood}^{\rm dry}$	$\lambda^{ ext{exp}}$		
	(as reported)		[1]	[K]	$\left[\mathrm{g/cm}^3\right]$	[W/(mK)]		
244	Western Red Cedar	trans	0.084	297.04	0.330	0.087	[86]	
245	Western Red Cedar	trans	0.051	297.04	0.431	0.118	[86]	
246	Western Red Cedar	trans	0.064	297.04	0.312	0.084	[86]	
$\frac{240}{247}$	White Ash	trans	0.004	297.04 297.04	0.512 0.678	0.168	[86]	
241	White Ash	trans	0.000	297.04 207.04	0.010	0.162	[86]	
240	White Ash	trans	0.031	297.04 207.04	0.000	0.102 0.147	[86]	
249 250	White Ash	trans	0.085	297.04 297.04	0.024	0.152	[86]	
200	White Ash	trong	0.000	207.04	0.570	0.125	[96]	
201	White Ash	trans	0.087	297.04 207.04	0.570	0.133 0.147	[00] [96]	
202	White Ash		0.080	297.04	0.304	0.147	[00] [06]	
200	White Ash	trans	0.081	297.04	0.470	0.131	[80] [96]	
204	White Fir	trans	0.088	297.04	0.323	0.082	[80]	
200	white Fir	trans	0.085	297.04	0.331	0.083	[80]	
256	White Fir	trans	0.084	297.04	0.332	0.085	[86]	
257	White Fir	trans	0.085	297.04	0.345	0.086	[86]	
258	White Fir	trans	0.084	297.04	0.357	0.086	[86]	
259	White Fir	trans	0.085	297.04	0.374	0.090	[86]	
260	White Fir	trans	0.085	297.04	0.391	0.096	[86]	
261	White Fir	trans	0.086	297.04	0.370	0.095	[86]	
262	White Fir	trans	0.084	297.04	0.402	0.100	[86]	
263	White Oak	trans	0.068	297.04	0.771	0.179	[86]	
264	White Oak	trans	0.073	297.04	0.658	0.170	[86]	
265	White Oak	trans	0.067	297.04	0.642	0.164	[86]	
266	White Oak	trans	0.069	297.04	0.599	0.157	[86]	
267	Northern White Pine	trans	0.063	297.04	0.489	0.127	[86]	
268	Northern White Pine	trans	0.068	297.04	0.469	0.131	[86]	
269	Northern White Pine	trans	0.062	297.04	0.421	0.109	[86]	
270	Northern White Pine	trans	0.069	297.04	0.402	0.115	[86]	
271	Northern White Pine	trans	0.067	297.04	0.402	0.115	[86]	
272	Northern White Pine	trans	0.066	297.04	0.368	0.102	[86]	
273	Northern White Pine	trans	0.614	297.04	0.237	0.095	[86]	
274	Northern White Pine	trans	0.065	297.04	0.346	0.096	[86]	
275	Northern White Pine	trans	0.063	297.04	0.317	0.096	[86]	
276	Yellow Birch	trans	0.097	297.04	0.662	0.147	[86]	
277	Yellow Birch	trans	0.091	297.04	0.645	0.145	[86]	
278	Vellow Birch	trans	0.001	207.01 297.04	0.609	0.139	[86]	
279	Yellow Birch	trans	0.002	297.01 297.04	0.552	0.124	[86]	
$\frac{219}{280}$	Red oak	R-trans	0.102	300.93	0.502 0.599	0.124 0.164	[111]	
-00 901	Rod only	R trans	0 1 / 9	300.05	0.500	0.164	[111]	
201 999	Red oak	R trans	0.140	300.99 300.99	0.399	0.104	[±±⊥] [111]	
202 202	Ded oak	n-traiis D	0.000	300.99 200.99	0.010	0.109	[111]	
200 901	Ded oak	n D trong	0.140	300.93 300.93	0.010	0.170	[111]	
204 205	neu oak Dod ool	n-trans	0.080	200.93 200.02	0.020	0.131	[111]	
280	neu oak	n-trans	0.083	200.93	0.020	0.104	[111]	

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No.	Species	Direction	MC	T	ρ ^{dry} ,	$\lambda^{ ext{exp}}$	
	(as reported)		[1]	[K]	$\left[g/cm^{3} \right]$	[W/(mK)]	
286	Red oak	R	0.084	300.93	0.630	0 163	[111]
287	Southern red oak	trans	0.117	300.93	0.620	0.147	[111]
288	Southern red oak	trans	0.081	300.93	0.630	0.136	[111]
$\frac{-00}{289}$	Southern red oak	R-trans	0.137	300.93	0.679	0.183	[111]
290	Southern red oak	trans	0.062	300.93	0.690	0.157	[111]
291	Southern red oak	trans	0.059	300.93	0.690	0.166	[111]
292	Southern red oak	R-trans	0.112	300.93	0.700	0.175	[111]
293	Southern red oak	R-trans	0.076	300.93	0.721	0.164	[111]
294	Southern red oak	R-trans	0.108	300.93	0.670	0.160	[111]
295	Southern red oak	R-trans	0.103	300.93	0.680	0.151	[111]
296	Southern red oak	trans	0.101	300.93	0.679	0.144	[111]
297	Southern red oak	trans	0.110	300.93	0.679	0.151	[111]
298	Southern red oak	trans	0.103	300.93	0.679	0.151	[111]
299	Southern red oak	trans	0.101	300.93	0.690	0.151	[111]
300	Southern red oak	R	0.134	300.93	0.620	0.153	[111]
301	Southern red oak	R	0.084	300.93	0.639	0.162	[111]
302	Southern red oak	R	0.097	300.93	0.639	0.170	[111]
303	Southern red oak	R	0.091	300.93	0.639	0.169	[111]
304	Southern red oak	R-trans	0.081	300.93	0.650	0.159	[111]
305	White oak	trans	0.150	300.93	0.580	0.162	[111]
306	White oak	trans	0.093	300.93	0.599	0.144	[111]
307	White oak	trans	0.089	300.93	0.610	0.150	[111]
308	White oak	R	0.150	300.93	0.641	0.182	[111]
309	White oak	R-trans	0.071	300.93	0.670	0.172	[111]
310	White oak	R	0.092	300.93	0.679	0.159	[111]
311	White oak	R	0.108	300.93	0.679	0.164	[111]
312	White oak	R	0.089	300.93	0.679	0.169	[111]
313	Paper birch	R-trans	0.146	300.93	0.540	0.138	[111]
314	Paper birch	R-trans	0.090	300.93	0.561	0.132	[111]
315	Paper birch	R-trans	0.094	300.93	0.561	0.135	[111]
316	Paper birch	R-trans	0.085	300.93	0.561	0.125	[111]
317	Paper birch	R-trans	0.087	300.93	0.561	0.136	[111]
318	Yellow birch	R-trans	0.147	300.93	0.580	0.146	[111]
319	Yellow birch	R-trans	0.096	300.93	0.590	0.131	[111]
320	Yellow birch	R-trans	0.071	300.93	0.590	0.136	[111]
321	Yellow birch	R-trans	0.070	300.93	0.590	0.142	[111]
322	Yellow birch	R-trans	0.070	300.93	0.590	0.141	[111]
323	Yellow birch	R-trans	0.069	300.93	0.590	0.139	[111]
324	Yellow birch	trans	0.088	300.93	0.601	0.131	[111]
325	Yellow birch	trans	0.105	300.93	0.601	0.131	[111]
326	Blue beech	R-trans	0.108	300.93	0.639	0.176	[111]
327	Blue beech	R-trans	0.116	300.93	0.639	0.176	[111]

Table 4.4 – continued from previous page

	Table 4	$4.4 - ext{continu}$	ued fron	n previou	s page	
No.	Species	Direction	MC	T	$\rho_{\rm wood}^{\rm dry}$	$\lambda^{ ext{exp}}$
	(as reported)		[1]	[K]	$[g/cm^3]$	[W/(m K)]
328	Blue beech	trans	0.115	300.93	0.650	0.167 [111]
329	Silver maple	trans	0.102	300.93	0.551	0.137 [111]
330	Silver maple	R	0.106	300.93	0.561	0.159 [111]
331	Striped maple	Т	0 111	300.93	0.490	0.125 [111]
332	Striped maple	T	0.111	300.93	0.490	0.126 [111] 0.128 [111]
333	Striped maple	Ť	0.114	300.93	0.509	0.120 [111] 0.134 [111]
334	Bigleaf maple	R	0.085	300.93	0.570	0.154 [111]
335	Bigleaf maple	R	0.097	300.93	0.580	0.166 [111]
336	Bigleaf maple	В	0 140	300.93	0.580	0.170 [111]
337	Bigleaf maple	R	0.140	300.93	0.500	0.170 [111] 0.157 [111]
338	Bigleaf maple	R	0.000	300.93	0.550	0.157 [111] 0.159 [111]
339	Bed ash	R-trans	0.015	300.93	0.550	0.105 [111] 0.126 [111]
340	Red ash	R-trans	0.091	300.93	0.500	0.120 [111] 0.132 [111]
2/1	Red ash	D trong	0.083	200.02	0.500	0.102 [111]
041 249	Red ash	R-trans	0.080	300.95	0.509	0.124 [111] 0.128 [111]
042 242	White ash	T	0.009	300.93	0.521 0.620	0.126 [111] 0.150 [111]
240	White ash	т Т	0.094	300.93	0.039	0.159 [111] 0.152 [111]
344 345	Ralsa	trans	0.000	300.93	0.039	0.155 [111] 0.055 [111]
040	Dalsa	uans	0.090	300.93	0.110	0.000 [111]
346	Balsa	trans	0.086	300.93	0.110	0.055 [111]
347	Balsa	trans	0.133	300.93	0.110	0.060 [111]
348	Balsa	trans	0.087	300.93	0.110	0.053 [111]
349	Balsa	trans	0.086	300.93	0.110	0.055 [111]
350	Balsa	trans	0.093	300.93	0.120	0.056 [111]
351	Western white pine	trans	0.147	300.93	0.370	0.104 [111]
352	Western white pine	trans	0.077	300.93	0.380	0.088 [111]
353	Western white pine	R	0.070	300.93	0.401	0.109 [111]
354	Loblolly pine	T-trans	0.162	300.93	0.521	0.156 [111]
355	Loblolly pine	trans	0.119	300.93	0.540	0.156 [111]
356	Loblolly pine	T-trans	0.116	300.93	0.549	0.150 [111]
357	Loblolly pine	R-trans	0.177	300.93	0.549	0.149 [111]
358	Loblolly pine	T-trans	0.210	300.93	0.561	0.176 [111]
359	Loblolly pine	T-trans	0.157	300.93	0.570	0.163 [111]
360	Loblolly pine	T-trans	0.123	300.93	0.580	0.147 [111]
361	Shortleaf pine	T-trans	0.131	300.93	0.530	0.147 [111]
362	Shortleaf pine	T-trans	0.160	300.93	0.530	0.149 [111]
363	Shortleaf pine	trans	0.113	300.93	0.540	0.139 [111]
364	Shortleaf pine	T-trans	0.132	300.93	0.561	0.156 [111]
365	Shortleaf pine	R-trans	0.109	300.93	0.630	0.150 [111]
366	Shortleaf pine	R-trans	0.129	300.93	0.650	0.177 [111]
367	Shortleaf pine	R-trans	0.144	300.93	0.490	0.144 [111]
368	Shortleaf pine	R-trans	0.089	300.93	0.500	0.129 [111]
369	Shortleaf pine	R	0.090	300.93	0.519	0.130 [111]
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No	Species	Direction	MC	T	o ^{dry} .	λ exp	
1.0.	(as reported)	Direction	[1]	[K]	$\left[\text{g/cm}^3 \right]$	[W/(mK)]	
370	Longleaf pine	trans	0.172	300.93	0.610	0.170	[111]
371	Longleaf pine	trans	0.146	300.93	0.620	0.167	[111]
372	Longleaf pine	T-trans	0.171	300.93	0.620	0.179	[111]
373	Longleaf pine	trans	0.133	300.93	0.630	0.164	[111]
374	Longleaf pine	trans	0.130	300.93	0.630	0.159	[111]
375	Longleaf pine	trans	0.122	300.93	0.639	0.164	[111]
376	Longleaf pine	T-trans	0.166	300.93	0.639	0.175	[111]
377	Longleaf pine	T-trans	0.144	300.93	0.650	0.185	[111]
378	Longleaf pine	trans	0.122	300.93	0.660	0.164	[111]
379	Northern white pine	R-trans	0.076	300.93	0.360	0.100	[111]
380	Northern white pine	R-trans	0.078	300.93	0.370	0.096	[111]
381	Northern white pine	R	0.140	300.93	0.401	0.116	[111]
382	Northern white pine	R	0.076	300.93	0.410	0.112	[111]
383	Northern white pine	R	0.059	300.93	0.410	0.103	[111]
384	Northern white pine	R	0.063	300.93	0.410	0.103	[111]
385	Northern white pine	R	0.074	300.93	0.410	0.108	[111]
386	Northern white pine	R	0.067	300.93	0.410	0.102	[111]
387	Northern white pine	T-trans	0.136	300.93	0.420	0.108	[111]
388	Northern white pine	T-trans	0.081	300.93	0.431	0.100	[111]
389	Northern white pine	T-trans	0.080	300.93	0.431	0.099	[111]
390	Northern white pine	R	0.067	300.93	0.431	0.100	[111]
391	Northern white pine	R	0.090	300.93	0.431	0.109	[111]
392	Northern white pine	R	0.068	300.93	0.431	0.103	[111]
393	Northern white pine	R	0.089	300.93	0.431	0.105	[111]
394	Northern white pine	R	0.143	300.93	0.431	0.117	[111]
395	Northern white pine	R	0.055	300.93	0.439	0.105	[111]
396	Northern white pine	R	0.077	300.93	0.439	0.115	[111]
397	Norway pine	R	0.149	300.93	0.410	0.122	[111]
398	Norway pine	R	0.145	300.93	0.410	0.119	[111]
399	Norway pine	R	0.082	300.93	0.420	0.110	[111]
400	Norway pine	R	0.081	300.93	0.420	0.117	[111]
401	Norway pine	R	0.076	300.93	0.429	0.109	[111]
402	Norway pine	R	0.070	300.93	0.429	0.112	[111]
403	Norway pine	R	0.072	300.93	0.429	0.113	[111]
404	Lodgepole pine	R	0.110	300.93	0.460	0.117	[111]
405	Lodgepole pine	R	0.148	300.93	0.481	0.131	[111]
406	Lodgepole pine	R	0.091	300.93	0.490	0.129	[111]
407	Lodgepole pine	R	0.097	300.93	0.490	0.126	[111]
408	Lodgepole pine	R	0.092	300.93	0.490	0.121	[111]
409	Ponderosa pine	R-trans	0.181	300.93	0.429	0.128	[111]
410	Ponderosa pine	R-trans	0.106	300.93	0.450	0.117	[111]
411	Ponderosa pine	R-trans	0.102	300.93	0.450	0.116	[111]
	*				Contin		

Table 4.4 – continued from previous page

	Table 4	$4.4 - ext{continu}$	ued from	ı previou	s page		
No.	Species	Direction	MC	T	$\rho_{\rm max}^{\rm dry}$	$\lambda^{ ext{exp}}$	
	(as reported)		[1]	[K]	$\left[\mathrm{g/cm}^3\right]$	$[\mathrm{W}/(\mathrm{m}\mathrm{K})]$	
412	Ponderosa pine	R-trans	0.098	300.93	0.469	0.121	[111]
413	Ponderosa pine	R-trans	0.072	300.93	0.469	0.116	[111]
414	Ponderosa pine	R	0.091	300.93	0.479	0.122	[111]
415	Ponderosa pine	R	0.084	300.93	0.479	0.121	[111]
416	Ponderosa pine	R	0.085	300.93	0.479	0.124	[111]
417	Limber pine	R	0.091	300.93	0.380	0.102	[111]
418	Limber pine	R	0.111	300.93	0.380	0.103	[111]
419	Limber pine	R	0.101	300.93	0.380	0.102	[111]
420	Limber pine	R	0.162	300.93	0.380	0.109	[111]
421	Limber pine	R	0.105	300.93	0.389	0.103	[111]
422	Lowland white fir	trans	0.086	300.93	0.441	0.109	[111]
423	Lowland white fir	trans	0.085	300.93	0.441	0.110	[111]
424	Lowland white fir	trans	0.050	300.93	0.450	0.099	[111]
425	Lowland white fir	trans	0.050	300.93	0.450	0.106	[111]
426	Lowland white fir	trans	0.050	300.93	0.450	0 111	[111]
427	Lowland white fir	trans	0.050	300.93	0.450	0.106	[111]
428	Lowland white fir	trans	0.144	300.93	0.450	0.112	[111]
429	Lowland white fir	trans	0.086	300.93	0.460	0.110	[111]
430	Lowland white fir	trans	0.116	300.93	0.469	0.122	[111]
431	Lowland white fir	R-trans	0 115	300.93	0.479	0.116	[111]
432	Lowland white fir	R	0.138	300.93	0.500	0.110 0.117	[111]
433	Lowland white fir	R.	0.086	300.93	0.521	0.110	[111]
434	Lowland white fir	R	0.083	300.93	0.521	0.110	[111]
435	Engelmann spruce	R-trans	0.092	300.93	0.420	0.094	[111]
/36	Engelmann spruce	R-trans	0.097	300.03	0.420	0.098	[111]
430	Engelmann spruce	R	0.037	300.93	0.420 0.429	0.090	[111]
438	Douglas fir	R	0.001	300.93	0.429 0.479	$0.001 \\ 0.115$	[111]
439	Douglas fir	R	0.070	300.93	0.490	0.115	[111]
440	Douglas fir	R	0.100	300.93	0.490	0.119	[111]
441	Douglas fir	R	0.140	300.03	0.490	0.131	[111]
111 1/19	Douglas fir	R	0.140	300.03	0.490	0.114	[111]
443	Douglas fir	R	0.073	300.93	0.500	0.114 0.115	[111]
444	Western red cedar	R-trans	0.010	300.93	0.290	0.083	[111]
445	Western red cedar	R-trans	0.151	300.93	0.290	0.090	[111]
116	Western red eeder	D trong	0.122	300.03	0.200	0.001	[111]
440 //7	Western red cedar	R	0.133	300.93	0.290	0.091	[±±±] [111]
<u>1</u> 11	Western red cedar	R	0.009	300.93	0.280	0.000	[±±±] [111]
<u>1</u> 10	Western red cedar	R	0.035	300.33	0.200	0.000	[±±±]
450	Western red cedar	R	0.005	300.93	0.290	0.081	[111]
150	Western red eader	D trang	0.075	200.02	0.200	0.001	[+++]
401 459	Southorn white adar	n-traiis R	0.070	300.93 300.03	0.300	0.084	[111]
404	Southern white cedar	11	0.190	900.99	0.230	0.099	「TTT」

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Chapter 5

Multiscale model for moisture diffusivity

In this chapter, a multiscale homogenization model for steady state moisture transport in wood is developed and validated. The model aims at prediction of macroscopic diffusion properties of clear wood samples from their microstructure and the physical properties of a few microscale constituents. In the preceding Chapter 4, the theoretical background and fundamentals of the model were presented, and its specification for the estimation of macroscopic thermal conductivities was shown. Now the model is applied to steady state moisture diffusion below the fiber saturation point. A suitable mathematical description of moisture diffusion on a molecular scale is not available at the moment, therefore the model starts on a scale of about 50 micrometers, where the wood cells form a honeycomblike structure. In a first homogenization step, the effective moisture transport behavior of the cell structure is determined from moisture diffusion properties of the cell walls and the (moist) air in lumens, respectively. Further homogenization steps account for the larger vessels that exist in hardwood species, the annual rings which are a succession of layers with different densities, and finally wood rays, that form pathways in the radial direction throughout the stem. The model validation rests on experiments as in the case of heat conduction: The macroscopic diffusion coefficients predicted based on tissue-independent diffusion properties of cell walls and lumens (input data set I) by the multiscale homogenization model for tissue-specific composition data (input data set II) are compared to corresponding experimentally determined tissue-specific diffusion coefficients under steady state conditions (experimental data set). As for thermal conductivity, the good agreement of model predictions and test data underlines the suitability of the presented multiscale model.

5.1 Introduction

Diffusion is the movement of a substance through another substance. In isothermal processes, this movement is driven by concentration gradients [see Eq. (3.16)]. The resulting flux from higher concentration to lower concentration is due to the strive for equilibrium. The presented multiscale model is limited to these conditions and furthermore to transport processes below the fiber saturation point: diffusion processes in wood below the FSP involve the movement of water vapor through the void structure and the movement of bound water through the cell walls.

In this chapter, only transport processes under steady state conditions are considered. Fluxes and concentrations in each material point do not change with time then, and the two phases of water in wood (bound water and water vapor) are in equilibrium (see Chapter 2). They can therefore be treated together, because knowing the concentration of one phase allows straightforward calculation of the concentration of the other phase by use of a sorption isotherm (e.g. according to the USDA Wood Handbook [107]). In case of diffusion as governing transport process, a steady state process is described by Fick's first law of diffusion [Eq. (3.29)].

The variability of macroscopic moisture diffusion coefficients is even wider than that of thermal conductivities [55]. Again, it originates from differences between wood tissues at the macro-, micro-, and nanoscale. This has already motivated multiscale modeling efforts for moisture transport in wood, e.g. by Siau [95] and Perré [77]. Their models for the estimation of moisture diffusivities in wood based on a single tracheid "unitcell" relate the macroscopic diffusion coefficients to apparent densities, temperatures, and moisture contents. The present model aims at an improved representation of the morphology of wood, resulting in a good prediction quality for macroscopic diffusion coefficients across different wood species, and a more appropriate formulation of the physical background.

The link between microscale characteristics and resulting properties at higher length scales is again established by means of homogenization. Since the structure of the governing equations of steady state moisture diffusion (Fick's first law of diffusion) and thermal conduction (Fourier's law) is the same, the same homogenization techniques can be used. Hence, continuum micromechanics and, for the annual ring structure, rules of mixture are applied as in the model for thermal conductivity in the previous chapter. Substitution of thermal conductivity tensors \mathbf{K} by corresponding moisture diffusivity tensors \mathbf{D} allows straightforward application of the basic considerations and relations as presented in Chapter 4. This is elaborated in detail for the formulated diffusion homogenization steps in Section 5.3. Besides the information provided in the previous chapter, more comprehensive descriptions of continuum micromechanics are given by Dormieux [15] and Zaoui [113].

5.2 Diffusion coefficients of cell wall and lumen

As mentioned before, the wide variability of macroscopic moisture diffusion properties of wood originates for the most part from differences in the microstructures of individual samples. Herein, we start from the scale of wood cells and represent the influences of cell structure and annual rings by means of a multiscale homogenization scheme. Moreover, also the variability of the diffusivity of the cell wall in consequence of variable moisture contents contributes to the macroscopic variability of moisture diffusion, as well as variable shares and arrangements of the microscale constituents cellulose, hemicellulose, and lignin. Contrary to the situation in heat transport, the moisture diffusivity of the cell wall cannot be derived from the diffusivities of these constituents by means of some homogenization technique. Rather, water acts as a constituent of the cell wall itself, and the diffusion process through the cell wall is influenced by the interaction of bound water with the solid constituents. Moreover, the properties of bound water are strongly dependent on its concentration, which might complicate or even hinder a continuum representation.

Through the cell walls, pits interconnecting adjacent lumens provide fast transport routes inside wood, especially in the longitudinal material direction. Most pits become aspirated during wood drying. Nevertheless, the small portion of remaining unaspirated pits allows water vapor to penetrate much faster through the open pathways into the wood sample and, thus, affects the overall diffusion behavior. Moreover, although a closed pit hinders the flow of liquid water, it is still much more permeable than the surrounding cell wall, as could be shown in own numerical simulations of a single pit (see Section 5.7 of this chapter). In steady state processes, the moisture concentrations of lumens and cell walls are in equilibrium also if unaspirated pits exist. Although the geometry of pits is known (see e.g. Siau [95]), the number of aspirated pits depends on several parameters, for example the density, drying history, wood species etc. So the "degree of aspiration" is very difficult to determine. Hence their effect is considered in a smeared manner by applying an increased cell wall diffusivity as compared to the cell wall material itself in the presented model.

The according diffusivity of the cell wall is formulated in terms of moisture content and temperature. Siau [95] proposes application of the Arrhenius equation in order to describe these influences. His widely-used relation for the transversal cell wall diffusivity $D_{\rm cwm,trans}$ reads as

$$D_{\rm cwm, trans, Siau} = D_0 \, \exp\left(-\frac{E_b}{R\,T}\right) = 7 \cdot 10^{-6} \, \exp\left(-\frac{38500 - 29000\,MC}{R\,T}\right) \quad [{\rm m}^2/{\rm s}],$$
(5.1)

with $R = 8.314472 \,\mathrm{J}\,\mathrm{mol}^{-1}\,\mathrm{K}^{-1}$ as the universal gas constant, T as the actual temperature in [K], and MC as the moisture content, which is specified in the conventional manner as mass of water in wood in relation to dry mass of wood. Eq. (5.1) was derived based on experimental results at a temperature of 26.7 °C. In order to consider the nonlinear dependence of the activation energy E_b on moisture content at smaller values of MC and to better reproduce experimental data reported by Kollmann [55] for spruce diffusivity at different temperatures, the following slightly modified relation was used in the present approach:

$$D_{\rm cwm, trans} = 1.832 \cdot 10^{-4} \, \exp\left(-\frac{43623 - 20625 \, MC - 1227 \, \ln MC}{R \, T}\right) \quad [{\rm m}^2/{\rm s}]. \tag{5.2}$$

For a temperature of 26.7 °C, Eqs. (5.1) and (5.2) provide nearly equal results. As already mentioned, this relation covers the influence of pits on the cell wall diffusivity.

The longitudinal cell wall diffusivity $D_{\text{cwm,long}}$ is calculated according to Siau [95] from the transverse one as

$$D_{\rm cwm, long} = 2.5 \, D_{\rm cwm, trans}. \tag{5.3}$$

The orthotropic second order diffusion tensor of the cell wall material, \mathbf{D}_{cwm} , therefore reads as

$$\mathbf{D}_{\rm cwm} = \begin{bmatrix} D_{\rm cwm, trans} & 0 & 0\\ 0 & D_{\rm cwm, trans} & 0\\ 0 & 0 & D_{\rm cwm, long} \end{bmatrix}.$$
 (5.4)

Below the fiber saturation point the lumens are filled with a mixture of air and water vapor. The diffusion coefficient of water vapor in moist air, \mathring{D}_{air} , was determined by a semi-empirical equation given by Schirmer [89]:

$$\mathring{D}_{\rm air} = 2.31 \cdot 10^{-5} \left(\frac{p_{\rm atm}}{p_{\rm atm} + p_v}\right) \left(\frac{T}{273.15}\right)^{1.81} \ [{\rm m}^2/{\rm s}],\tag{5.5}$$

with p_{atm} denoting the atmospheric pressure, p_v the vapor pressure, and T the actual temperature in [K]. The diffusion behavior of air is isotropic, therefore the diffusion tensor of air used in the model reads as:

$$\check{\mathbf{D}}_{\mathrm{air}} = \check{D}_{\mathrm{air}} \,\mathbf{I},\tag{5.6}$$

where **I** denotes the second order unity tensor.

5.3 Definition of the multiscale homogenization model

In consequence of the analogous structure of the governing equations of steady state moisture diffusion and thermal conduction and the use of the same homogenization techniques, the multiscale homogenization model derived for thermal conduction in the previous chapter can be easily adapted to diffusion. The first two steps of the homogenization model for thermal conductivity account for the mixture of hemicellulose, lignin, and cellulose in the cell wall, resulting in a homogenized thermal conductivity of the cell wall material. Since the diffusion coefficient of the cell wall material marks the starting point of the homogenization model for moisture diffusion coefficients, only steps III to VI of the multiscale model for thermal conductivity are required here. This yields a four-level homogenization procedure as shown in Fig. 5.1.

In addition, particular attention was paid to the precise formulation of the conversion of the particular diffusion tensors from one representative volume element to the other.

It is obvious that the morphological parameters and phase volume fractions of the various homogenization steps are independent of the homogenized material property. Therefore densities, volume fractions, and aspect ratios of the single phases can be directly taken from Chapter 4.



Figure 5.1: Four-level homogenization procedure for diffusion coefficients of wood

5.3.1 Step III(a) / Step III(b) / Step III(c): Earlywood, latewood, ray cells

In step III(a) the wood cell structure of earlywood is reproduced by embedding ellipsoids (representing lumens filled with moist air) into a matrix material (representing the cell walls with diffusivities as described before). A Mori-Tanaka scheme is employed as homogenization method in the framework of continuum micromechanics. Substituting the moisture diffusion tensor of the cell wall material and the lumens, $\hat{\mathbf{D}}_{cwm}$ and $\hat{\mathbf{D}}_{air}$, respectively, for the corresponding thermal conductivity tensors \mathbf{K}_{cwm}^{MT} and \mathbf{K}_{air} in Eq. (4.19), yields the effective diffusion tensor of earlywood $\hat{\mathbf{D}}_{early}^{MT}$ as

$$\hat{\mathbf{D}}_{\text{early}}^{\text{MT}} = \left\{ \hat{f}_{\text{cwm}} \hat{\mathbf{D}}_{\text{cwm}} + \hat{f}_{\text{lum}} \hat{\mathbf{D}}_{\text{air}} \cdot \left[\mathbf{I} + \mathbf{P}_{\text{ell,early}}^{\text{cwm}} \cdot \left(\hat{\mathbf{D}}_{\text{air}} - \hat{\mathbf{D}}_{\text{cwm}} \right) \right]^{-1} \right\} \cdot \left\{ \hat{f}_{\text{cwm}} \mathbf{I} + \hat{f}_{\text{lum}} \left[\mathbf{I} + \mathbf{P}_{\text{ell,early}}^{\text{cwm}} \cdot \left(\hat{\mathbf{D}}_{\text{air}} - \hat{\mathbf{D}}_{\text{cwm}} \right) \right]^{-1} \right\}^{-1}, \quad (5.7)$$

with f_{cwm} and $\overline{f}_{\text{lum}}$ denoting the volume fractions of cell wall material and lumens, respectively. The Hill tensor $\mathbf{P}_{\text{ell,early}}^{\text{cwm}}$ accounts for the ellipsoidal shape of the lumens.

The effective diffusion tensor of earlywood $\hat{\mathbf{D}}_{early}^{MT}$ relates the effective moisture flux to the gradient of moisture concentration in earlywood. In contrast, the diffusion tensors of cell wall material and air specified in Section 5.2, \mathbf{D}_{cwm} and $\hat{\mathbf{D}}_{air}$, are based on a gradient of moisture concentration in pure cell wall material and pure air, respectively. Therefore these two diffusion tensors have to be expressed in terms of moisture concentration gradients in earlywood. The resulting flux is the same, irrespective of the reference volume chosen for the concentration gradient. Fick's first law of diffusion gives a relation between these two diffusion coefficients of moisture in air: \mathbf{D}_{air} , based on a gradient of moisture concentration in air and \mathbf{D}_{air} , based on a gradient of moisture concentration in earlywood:

$$\mathbf{J} = -\mathring{\mathbf{D}}_{\mathrm{air}} \frac{\partial \frac{\mathring{m}_{\mathrm{H_2O}}}{V_{\mathrm{air}}}}{\partial \mathbf{x}} = -\widehat{\mathbf{D}}_{\mathrm{air}} \frac{\partial \frac{\widehat{m}_{\mathrm{H_2O}}}{V_{\mathrm{early}}}}{\partial \mathbf{x}},\tag{5.8}$$

with V_{air} and V_{early} as the volumes of lumens and earlywood and $\hat{m}_{\text{H}_2\text{O}}$ and $\hat{m}_{\text{H}_2\text{O}}$ as the mass of water, contained in these volumes of lumens and earlywood, respectively. Reformulating the second and third term in Eq. (5.8) for $\hat{\mathbf{D}}_{\text{air}}$ yields

$$\hat{\mathbf{D}}_{air} = \overset{\circ}{\mathbf{D}}_{air} \frac{\partial \frac{\mathring{m}_{H_2O}}{V_{air}}}{\partial \frac{\mathring{m}_{H_2O}}{V_{early}}} = \overset{\circ}{\mathbf{D}}_{air} \frac{\frac{\partial \mathring{m}_{H_2O}}{V_{air}}}{\widehat{f}_{lum} \frac{\partial \mathring{m}_{H_2O}}{V_{air}} + \widehat{f}_{cwm} \frac{\partial m_{H_2O}}{V_{cwm}}} = \overset{\circ}{\mathbf{D}}_{air} \frac{1}{\widehat{f}_{lum} + \widehat{f}_{cwm} \frac{\partial m_{H_2O}}{\partial \mathring{m}_{H_2O}} \frac{V_{air}}{V_{cwm}}},$$

$$(5.9)$$

with $m_{\rm H_2O}$ denoting the mass of water in the cell walls within a volume of $V_{\rm cwm}$.

The term $\frac{\partial m_{\rm H_2O}}{\partial \tilde{m}_{\rm H_2O}} \frac{V_{\rm air}}{V_{\rm cwm}}$ in Eq. (5.9) can be further evaluated by use of a sorption isotherm, which is usually specified in terms of moisture content MC of wood and relative humidity φ in the surrounding air. In order to relate the mass of water in the lumens $\mathring{m}_{\rm H_2O}$ to relative humidity φ , the ideal gas law is invoked:

$$p_v = p_{v,\text{sat}} \varphi = \frac{\mathring{n}_{\text{H}_2\text{O}}}{V_{\text{air}}} R T = \frac{\mathring{m}_{\text{H}_2\text{O}} R T}{V_{\text{air}} M_{\text{H}_2\text{O}}},$$
(5.10)

where $\mathring{n}_{\text{H}_{2}\text{O}}$ is the amount of vapor in the air volume V_{air} , R the universal gas constant introduced before, and $M_{\text{H}_{2}\text{O}} = 18.01528 \text{ g/mol}$ the molecular weight of water. The saturated water pressure $p_{v,\text{sat}}$ can be calculated depending on temperature T by a fitted polynomial taken from Schmidt [90]:

$$p_{v,\text{sat}} = 2.2064 \cdot 10^7 \exp\left[\frac{647.14}{T \,[\text{K}]} \left(-7.85823\tau + 1.83991\tau^{1.5} -11.7811\tau^3 + 22.6705\tau^{3.5} - 15.9393\tau^4 + 1.77516\tau^{7.5}\right)\right] \quad [\text{Pa}],$$
(5.11)

with

$$\tau = 1 - \frac{T\left[K\right]}{647.14}.$$
(5.12)

Rewriting Eq. (5.10) yields the mass of water in air \mathring{m}_{H_2O} as a function of relative humidity φ :

$$\mathring{m}_{\rm H_2O} = \frac{p_{v,\rm sat} M_{\rm H_2O}}{R T} V_{\rm air} \varphi.$$
(5.13)

The mass of water in the cell wall, $m_{\rm H_2O}$, can be expressed as function of moisture content MC as

$$m_{\rm H_2O} = \rho_{\rm cwm}^{\rm dry} V_{\rm cwm}^{\rm dry} MC = \rho_{\rm cwm}^{\rm dry} \left(1 - \tilde{f}_{\rm H_2O} f_{\rm poly}\right) V_{\rm cwm} MC, \tag{5.14}$$

with $\rho_{\text{cwm}}^{\text{dry}}$ as the dry mass density of the cell wall material, $\tilde{f}_{\text{H}_2\text{O}}$ as the volume fraction of water in the polymer network, and f_{poly} as the volume fraction of polymer network in the moist cell wall material (see Chapter 4). Substituting Eqs. (5.13) and (5.14) in Eq. (5.9) yields finally

$$\hat{\mathbf{D}}_{air} = \mathbf{D}_{air} \frac{1}{\hat{f}_{lum} + \hat{f}_{cwm} \frac{\rho_{cwm}^{dry} (1 - \tilde{f}_{H_2O} f_{poly}) RT}{p_{v,sat} M_{H_2O}} \frac{\partial MC}{\partial \varphi}}.$$
(5.15)

The term $\frac{\partial MC}{\partial \varphi}$ denotes the slope of the sorption isotherm. In the model calculations the sorption data given in the USDA Wood Handbook [107] was used for its determination. This data is averaged over test results for different wood species as well as over adsorption and desorption data, respectively. If available, use of sorption data determined for a specific specimen of wood will increase the accuracy of the predictions by the multiscale model.

Similar to the diffusion coefficient of air, also the cell wall diffusion coefficient \mathbf{D}_{cwm} , which is based on a concentration gradient of water in the cell wall, has to be converted into a diffusion coefficient $\hat{\mathbf{D}}_{cwm}$ based on a concentration gradient in earlywood. In analogy to Eq. (5.9) this conversion reads mathematically as

$$\hat{\mathbf{D}}_{\text{cwm}} = \mathbf{D}_{\text{cwm}} \frac{1}{\hat{f}_{\text{cwm}} + \hat{f}_{\text{lum}} \frac{\partial \mathring{m}_{\text{H}_2\text{O}}}{\partial m_{\text{H}_2\text{O}}} \frac{V_{\text{cwm}}}{V_{\text{air}}}}.$$
(5.16)

Substituting Eqs. (5.13) and (5.14) in Eq. (5.16) yields

$$\hat{\mathbf{D}}_{\text{cwm}} = \mathbf{D}_{\text{cwm}} \frac{1}{\hat{f}_{\text{cwm}} + \hat{f}_{\text{lum}} \frac{p_{v,\text{sat}} M_{\text{H}_{2}\text{O}}}{\rho_{\text{cwm}}^{\text{dry}} (1 - \tilde{f}_{\text{H}_{2}\text{O}} f_{\text{poly}}) R T} \frac{\partial \varphi}{\partial M C}}.$$
(5.17)

The second term in the denominator of Eq. (5.17) is very small compared to f_{cwm} , so that Eq. (5.17) reduces in good approximation to

$$\hat{\mathbf{D}}_{\rm cwm} \approx \mathbf{D}_{\rm cwm} \frac{1}{\hat{f}_{\rm cwm}}.$$
(5.18)

Steps III(b) and III(c) are performed analogously to step III(a) with according morphological characteristics of the cells in latewood and ray tissue, and results in effective properties of latewood and ray cells.

5.3.2 Step IV: Hardwood with vessels

In case of hardwood, step IV is used to include additional large vessels that mainly appear in earlywood. Again a Mori-Tanaka scheme is used, this time with cylindrical inclusions representing the vessels oriented in the longitudinal direction of wood, and also filled with moist air. Starting again from the corresponding equation (4.22) for thermal conduction in Chapter 4, substitution of $\bar{\mathbf{D}}_{\text{early}}^{\text{MT}}$ and $\bar{\mathbf{D}}_{\text{air}}$ for $\mathbf{K}_{\text{early}}^{\text{MT}}$ and \mathbf{K}_{air} results in

$$\bar{\mathbf{D}}_{\text{hard}+\text{ves}}^{\text{MT}} = \left\{ \bar{f}_{\text{early}} \bar{\mathbf{D}}_{\text{early}}^{\text{MT}} + \bar{f}_{\text{ves}} \bar{\mathbf{D}}_{\text{air}} \cdot \left[\mathbf{I} + \mathbf{P}_{\text{circcyl}}^{\text{early}} \cdot \left(\bar{\mathbf{D}}_{\text{air}} - \bar{\mathbf{D}}_{\text{early}}^{\text{MT}} \right) \right]^{-1} \right\} \cdot \left\{ \bar{f}_{\text{early}} \mathbf{I} + \bar{f}_{\text{ves}} \left[\mathbf{I} + \mathbf{P}_{\text{circcyl}}^{\text{early}} \cdot \left(\bar{\mathbf{D}}_{\text{air}} - \bar{\mathbf{D}}_{\text{early}}^{\text{MT}} \right) \right]^{-1} \right\}^{-1}, \quad (5.19)$$

with \bar{f}_{early} and \bar{f}_{ves} denoting the volume fractions of earlywood and vessels in their combined tissue, respectively. The Hill tensor $\mathbf{P}_{circcyl}^{early}$ accounts for the circular cylindrical shape of the vessels in earlywood.

Again the reference volume for the concentration changes during the homogenization step, this time to the volume of hardwood with vessels. Therefore the diffusion tensors of earlywood and air, $\hat{\mathbf{D}}_{\text{early}}^{\text{MT}}$ and $\hat{\mathbf{D}}_{\text{air}}$, have to be expressed in terms of concentrations in hardwood with vessels. In analogy to Eq. (5.9) this is done for the diffusion tensor of air by

$$\bar{\mathbf{D}}_{\mathrm{air}} = \mathring{\mathbf{D}}_{\mathrm{air}} \frac{1}{\bar{f}_{\mathrm{ves}} + \bar{f}_{\mathrm{early}} \frac{\partial \hat{m}_{\mathrm{H_2O}}}{\partial \mathring{m}_{\mathrm{H_2O}} \frac{V_{\mathrm{air}}}{V_{\mathrm{early}}}}.$$
(5.20)

Neglecting the minor contribution of the water in the lumens, the mass of water in earlywood $\hat{m}_{\rm H_2O}$ can be approximately expressed as function of moisture content MC as

$$\hat{m}_{\rm H_2O} \approx \rho_{\rm cwm}^{\rm dry} \left(1 - \tilde{f}_{\rm H_2O} f_{\rm poly} \right) \hat{f}_{\rm cwm} V_{\rm early} MC.$$
(5.21)

Substituting Eqs. (5.13) and (5.21) in Eq. (5.20) yields

$$\bar{\mathbf{D}}_{\text{air}} \approx \mathring{\mathbf{D}}_{\text{air}} \frac{1}{\bar{f}_{\text{ves}} + \bar{f}_{\text{early}} \frac{\rho_{\text{cwm}}^{\text{dry}} \left(1 - \tilde{f}_{\text{H}_2 \text{O}} f_{\text{poly}}\right) \hat{f}_{\text{cwm}} R T}{p_{v, \text{sat}} M_{\text{H}_2 \text{O}}} \frac{\partial M C}{\partial \varphi}}.$$
(5.22)

Similar to the diffusion coefficient of air also the earlywood diffusion coefficient $\hat{\mathbf{D}}_{\text{early}}^{\text{MT}}$, which is originally based on a concentration gradient of water in earlywood, has to be converted to a diffusion coefficient $\bar{\mathbf{D}}_{\text{early}}^{\text{MT}}$, based on a concentration gradient in hardwood with vessels. In analogy to Eq. (5.20) this is done by

$$\bar{\mathbf{D}}_{\text{early}}^{\text{MT}} = \hat{\mathbf{D}}_{\text{early}}^{\text{MT}} \frac{1}{\hat{f}_{\text{early}} + \hat{f}_{\text{ves}} \frac{\partial \mathring{m}_{\text{H}_2\text{O}}}{\partial \widehat{m}_{\text{H}_2\text{O}}} \frac{V_{\text{early}}}{V_{\text{air}}}}.$$
(5.23)

Neglecting again the water in the lumens and substituting Eqs. (5.13) and (5.21) in Eq. (5.23) yields

$$\bar{\mathbf{D}}_{\text{early}}^{\text{MT}} \approx \hat{\mathbf{D}}_{\text{early}}^{\text{MT}} \frac{1}{\hat{f}_{\text{early}} + \hat{f}_{\text{ves}} \frac{p_{v,\text{sat}} M_{\text{H}_2\text{O}}}{\rho_{\text{cvm}}^{\text{dry}} (1 - \tilde{f}_{\text{H}_2\text{O}} f_{\text{poly}}) \hat{f}_{\text{cvm}} R T} \frac{\partial \varphi}{\partial M C}}.$$
(5.24)

As before, the second term in the denominator of Eq. (5.24) is very small compared to \hat{f}_{early} , so that Eq. (5.24) reduces in good approximation to

$$\bar{\mathbf{D}}_{\text{early}}^{\text{MT}} \approx \hat{\mathbf{D}}_{\text{early}}^{\text{MT}} \frac{1}{\hat{f}_{\text{early}}}.$$
(5.25)

5.3.3 Step V: Annual rings

Step V accounts for the layered configuration of earlywood and latewood, that is visible as annual rings on the macroscale. In the longitudinal and tangential direction the moisture fluxes of the two materials act in parallel, while in the radial direction they are connected in series. Reformulating Eqs. (4.24) in Chapter 4 for moisture diffusion with $\ddot{\mathbf{D}}_{\text{ann}}^{\text{S/P}}$, $\ddot{\mathbf{D}}_{\text{hard+ves}}^{\text{MT}}$, and $\ddot{\mathbf{D}}_{\text{late}}^{\text{MT}}$ instead of $\mathbf{K}_{\text{ann}}^{\text{S/P}}$, $\mathbf{K}_{\text{hard+ves}}^{\text{MT}}$, and $\mathbf{K}_{\text{late}}^{\text{MT}}$ yields the non-zero components of $\ddot{\mathbf{D}}_{\text{ann}}^{\text{S/P}}$ as

$$\ddot{D}_{\text{ann},11}^{\text{S/P}} = \left(\ddot{f}_{\text{hard}+\text{ves}}/\ddot{D}_{\text{hard}+\text{ves},11}^{\text{MT}} + \ddot{f}_{\text{late}}/\ddot{D}_{\text{late},11}^{\text{MT}}\right)^{-1},$$

$$\ddot{D}_{\text{ann},22}^{\text{S/P}} = \ddot{f}_{\text{hard}+\text{ves}}\ddot{D}_{\text{hard}+\text{ves},22}^{\text{MT}} + \ddot{f}_{\text{late}}\ddot{D}_{\text{late},22}^{\text{MT}},$$

$$\ddot{D}_{\text{ann},33}^{\text{S/P}} = \ddot{f}_{\text{hard}+\text{ves}}\ddot{D}_{\text{hard}+\text{ves},33}^{\text{MT}} + \ddot{f}_{\text{late}}\ddot{D}_{\text{late},33}^{\text{MT}},$$
(5.26)

with $\ddot{f}_{hard+ves}$ and \ddot{f}_{late} denoting the volume fractions of hardwood with vessels and latewood, respectively, in the layered wood material across the annual rings. As long as the reference coordinate system is chosen parallel and perpendicular to the layers, and, thus, to the principal material directions, the off-diagonal tensor components vanish.

As in the previous steps, the diffusion tensors of hardwood with vessels and of latewood have to be expressed in terms of concentration gradients in the annual rings. Via adapting Eq. (5.9), this is done by

$$\ddot{\mathbf{D}}_{\text{hard}+\text{ves}}^{\text{MT}} = \bar{\mathbf{D}}_{\text{hard}+\text{ves}}^{\text{MT}} \frac{1}{\ddot{f}_{\text{hard}+\text{ves}} + \ddot{f}_{\text{late}}} \frac{\partial \check{m}_{\text{H}_2\text{O}}}{\partial \bar{m}_{\text{H}_2\text{O}}} \frac{V_{\text{hard}+\text{ves}}}{V_{\text{late}}}.$$
(5.27)

Neglecting again the water contained in the lumens, the mass of water in latewood $\check{m}_{\rm H_2O}$ and the mass of water in hardwood with vessels, $\bar{m}_{\rm H_2O}$, can be approximately expressed as functions of moisture content MC alone as

$$\check{m}_{\rm H_2O} \approx \rho_{\rm cwm}^{\rm dry} \left(1 - \tilde{f}_{\rm H_2O} f_{\rm poly} \right) \check{f}_{\rm cwm} V_{\rm late} MC, \tag{5.28}$$

$$\bar{m}_{\rm H_2O} \approx \rho_{\rm cwm}^{\rm dry} \left(1 - \tilde{f}_{\rm H_2O} f_{\rm poly}\right) \bar{f}_{\rm early} \, \hat{f}_{\rm cwm} \, V_{\rm hard+ves} \, MC.$$
(5.29)

Substituting Eqs. (5.28) and (5.29) in Eq. (5.27) yields the approximate relation

$$\ddot{\mathbf{D}}_{\text{hard}+\text{ves}}^{\text{MT}} \approx \bar{\mathbf{D}}_{\text{hard}+\text{ves}}^{\text{MT}} \frac{1}{\ddot{f}_{\text{hard}+\text{ves}} + \ddot{f}_{\text{late}} \frac{\check{f}_{\text{cwm}}}{\bar{f}_{\text{early}} \hat{f}_{\text{cwm}}}}.$$
(5.30)

The conversion of the diffusion coefficient of latewood is carried out analogously as:

$$\ddot{\mathbf{D}}_{\text{late}}^{\text{MT}} = \check{\mathbf{D}}_{\text{late}}^{\text{MT}} \frac{1}{\ddot{f}_{\text{late}} + \ddot{f}_{\text{hard}+\text{ves}} \frac{\partial \bar{m}_{\text{H}_2\text{O}}}{\partial \check{m}_{\text{H}_2\text{O}}} \frac{V_{\text{late}}}{V_{\text{hard}+\text{ves}}}}.$$
(5.31)

Substituting Eqs. (5.28) and (5.29) in Eq. (5.31) finally yields

$$\ddot{\mathbf{D}}_{\text{late}}^{\text{MT}} \approx \check{\mathbf{D}}_{\text{late}}^{\text{MT}} \frac{1}{\ddot{f}_{\text{late}} + \ddot{f}_{\text{hard}+\text{ves}} \frac{\bar{f}_{\text{early}} \hat{f}_{\text{cwm}}}{\bar{f}_{\text{cwm}}}}.$$
(5.32)

5.3.4 Step VI: Clear wood sample

In the last step the wood rays are included in the annual ring material of the previous step in order to complete the homogenization procedure. These additional pathways for moisture transport in the radial direction are represented by ellipsoidal cylinders, consisting of the material of homogenization step III(c). Substituting $\mathbf{K}_{\text{wood}}^{\text{MT}}$, $\mathbf{K}_{\text{ann}}^{\text{S/P}}$, and $\mathbf{K}_{\text{ray}}^{\text{MT}}$ by $\mathbf{\acute{D}}_{\text{wood}}^{\text{MT}}$, $\mathbf{\acute{D}}_{\text{ann}}^{\text{S/P}}$, and $\mathbf{\acute{D}}_{\text{ray}}^{\text{MT}}$ in Eq. (4.25) of Chapter 4 finally results in the sought estimate for the homogenized moisture diffusion tensor of clear wood:

$$\hat{\mathbf{D}}_{\text{wood}}^{\text{MT}} = \left\{ \hat{f}_{\text{ann}} \hat{\mathbf{D}}_{\text{ann}}^{\text{S/P}} + \hat{f}_{\text{ray}} \hat{\mathbf{D}}_{\text{ray}}^{\text{MT}} \cdot \left[\mathbf{I} + \mathbf{P}_{\text{ellcyl}}^{\text{ann}} \cdot \left(\hat{\mathbf{D}}_{\text{ray}}^{\text{MT}} - \hat{\mathbf{D}}_{\text{ann}}^{\text{S/P}} \right) \right]^{-1} \right\} \cdot \left\{ \hat{f}_{\text{ann}} \mathbf{I} + \hat{f}_{\text{ray}} \left[\mathbf{I} + \mathbf{P}_{\text{ellcyl}}^{\text{ann}} \cdot \left(\hat{\mathbf{D}}_{\text{ray}}^{\text{MT}} - \hat{\mathbf{D}}_{\text{ann}}^{\text{S/P}} \right) \right]^{-1} \right\}^{-1}.$$

$$(5.33)$$

with f_{ann} and f_{ray} denoting the volume fractions of annual rings and wood rays, respectively. The Hill tensor $\mathbf{P}_{\text{ellcyl}}^{\text{ann}}$ accounts for the elliptic cylindrical shape of the wood rays in the annual rings.

As before, the reference volume for the concentration is changed during the homogenization step. Therefore the diffusion tensors of annual rings and rays have to be expressed in terms of concentrations in wood. In analogy to Eq. (5.9) this is performed again for the diffusion tensor of the annual ring material by

$$\dot{\mathbf{D}}_{\mathrm{ann}}^{\mathrm{S/P}} = \ddot{\mathbf{D}}_{\mathrm{ann}}^{\mathrm{S/P}} \frac{1}{\dot{f}_{\mathrm{ann}} + \dot{f}_{\mathrm{ray}} \frac{\partial \dot{m}_{\mathrm{H}_{2}\mathrm{O}}}{\partial \ddot{m}_{\mathrm{H}_{2}\mathrm{O}}} \frac{V_{\mathrm{ann}}}{V_{\mathrm{ray}}}}.$$
(5.34)

Neglecting the water in the lumens, the mass of water in the annual rings $\ddot{m}_{\rm H_2O}$ and the mass of water in the rays $\dot{m}_{\rm H_2O}$ can be expressed as functions of moisture content MC in good approximation as

$$\dot{m}_{\rm H_2O} \approx \rho_{\rm cwm}^{\rm dry} \left(1 - \tilde{f}_{\rm H_2O} f_{\rm poly} \right) \dot{f}_{\rm cwm} V_{\rm ray} MC, \tag{5.35}$$

$$\ddot{m}_{\rm H_2O} \approx \rho_{\rm cwm}^{\rm dry} \left(1 - \tilde{f}_{\rm H_2O} f_{\rm poly}\right) \left(\ddot{f}_{\rm hard+ves} \bar{f}_{\rm early} \hat{f}_{\rm cwm} + \ddot{f}_{\rm late} \check{f}_{\rm cwm}\right) V_{\rm ann} MC.$$
(5.36)

Substituting Eqs. (5.35) and (5.36) in Eq. (5.34) yields

$$\dot{\mathbf{D}}_{\mathrm{ann}}^{\mathrm{S/P}} \approx \ddot{\mathbf{D}}_{\mathrm{ann}}^{\mathrm{S/P}} \frac{1}{\hat{f}_{\mathrm{ann}} + \hat{f}_{\mathrm{ray}} \frac{\hat{f}_{\mathrm{cwm}}}{\bar{f}_{\mathrm{hard}+\mathrm{ves}} \bar{f}_{\mathrm{early}} \hat{f}_{\mathrm{cwm}} + \ddot{f}_{\mathrm{late}} \tilde{f}_{\mathrm{cwm}}}}.$$
(5.37)

The density of wood rays was set equal to the mean density of the wood sample (see Chapter 4), therefore – assuming the same cell wall material as in earlywood and late-wood – the volume fraction of cell wall material in the ray cells is the same as in the annual rings:

$$\dot{f}_{\rm cwm} = \underbrace{\ddot{f}_{\rm hard+ves}\,\bar{f}_{\rm early}\,\hat{f}_{\rm cwm} + \ddot{f}_{\rm late}\,\check{f}_{\rm cwm}}_{\ddot{f}_{\rm cwm}}.$$
(5.38)

With this relation, Eq. (5.37) reduces to

$$\dot{\mathbf{D}}_{\mathrm{ann}}^{\mathrm{S/P}} \approx \ddot{\mathbf{D}}_{\mathrm{ann}}^{\mathrm{S/P}} \frac{1}{\dot{f}_{\mathrm{ann}} + \dot{f}_{\mathrm{ray}}} = \ddot{\mathbf{D}}_{\mathrm{ann}}^{\mathrm{S/P}}.$$
(5.39)

Finally, the conversion of the ray cell diffusion coefficient follows from

$$\dot{\mathbf{D}}_{\mathrm{ray}}^{\mathrm{MT}} \approx \dot{\mathbf{D}}_{\mathrm{ray}}^{\mathrm{MT}} \frac{1}{\dot{f}_{\mathrm{ray}} + \dot{f}_{\mathrm{ann}} \frac{\partial \ddot{m}_{\mathrm{H_2O}}}{\partial \dot{m}_{\mathrm{H_2O}}} \frac{V_{\mathrm{ray}}}{V_{\mathrm{ann}}}}.$$
(5.40)

Substituting Eqs. (5.35) and (5.36) in Eq. (5.40) and considering Eq. (5.38) yields

$$\dot{\mathbf{D}}_{\mathrm{ray}}^{\mathrm{MT}} \approx \dot{\mathbf{D}}_{\mathrm{ray}}^{\mathrm{MT}} \frac{1}{\acute{f}_{\mathrm{ray}} + \acute{f}_{\mathrm{ann}} \frac{\ddot{f}_{\mathrm{hard} + \mathrm{ves}} \bar{f}_{\mathrm{early}} \hat{f}_{\mathrm{cwm}} + \ddot{f}_{\mathrm{late}} \check{f}_{\mathrm{cwm}}}{\acute{f}_{\mathrm{cwm}}}}$$
(5.41)

$$= \dot{\mathbf{D}}_{\mathrm{ray}}^{\mathrm{MT}} \frac{1}{\dot{f}_{\mathrm{ray}} + \dot{f}_{\mathrm{ann}} 1} = \dot{\mathbf{D}}_{\mathrm{ray}}^{\mathrm{MT}}.$$
(5.42)

5.4 Experimental validation

Pursuing the same strategy as for the thermal conductivity predictions, validation of the developed multiscale model for steady state diffusion is based on experimental data from literature. In particular, model predictions for diffusion coefficients, computed based on sample-independent diffusivities of cell wall material and air (input data set I) for given sample-specific volume fractions and morphological properties (input data set II), are compared with corresponding experimental results measured under steady state conditions (experimental data set).

Required sample-specific input data for the model are wood species, moisture content, temperature, and the dry mass density of the sample. In order to accomplish the comparison, also knowledge of the direction of measurement is needed. Therefore only those experimental results with all these values reported were used, resulting in 190 complete data sets (from Kollmann [55], Sehlstedt-Persson [94], Comstock [11], and Choong [10]).

The comparison is illustrated in Fig. 5.2, where each marker indicates one pair of a measured diffusion coefficient and the corresponding model prediction. Different markers are used for softwood and hardwood and for the three principal material directions L, R, and T, respectively. Due to the wide range of values a log-log plot is used. The solid diagonal line indicates perfect agreement between model predicted and experimental values.

In order to quantify the agreement, differences between model estimates and experimental measurements are determined in terms of mean values and standard deviations of relative prediction errors \bar{e} and s. Beside these error measures, correlation coefficients r^2 are determined. Error measures as well as correlation coefficients are summarized in Table 5.1 for exclusively softwood samples, exclusively hardwood samples, and for all samples.

The model estimates for the diffusion coefficients in radial, tangential, and longitudinal direction, $\mathbf{\hat{D}}_{\text{wood}}^{\text{MT}}$, show a good agreement with the corresponding measured values $\mathbf{\hat{D}}_{\text{wood}}^{\text{exp}}$. The correlation coefficient of the diffusion coefficients of $r^2 = 98.0\%$ across all samples and material directions is very good. The mean errors of \bar{e} show a slight overestimation of the diffusion coefficient by the model for softwood, but an underestimation for hardwood. This could indicate a systematic error of the model. However, all data of hardwood specimens are taken from only one literature source, so that more hardwood specimens, particularly from different experimental campaigns, should be taken



Figure 5.2: Comparison of predicted and measured diffusion coefficients

Table 5.1: Agreement of model predictions and experimental results of moisture diffusion coefficients of wood: Correlation coefficients and error measures.

	r^2	\bar{e}	s
Softwood samples	97.9%	+4.8%	20.5%
Hardwood samples	83.4%	-19.5%	12.6%
All samples	98.0%	+2.0%	21.3%

into account before drawing such conclusions. Data for softwood specimens origin from three different literature sources and incorporates 168 samples from three different wood species, which provides a good basis for validating the model and for confirming its good predictive capabilities.

The standard deviations of relative prediction errors s display the spreading of the prediction errors. A possible reason for the observed deviations of the model predictions from the experimental results is the negligence of the influence of the chemical composition of the cell wall and of the degree of pit aspiration on the supposed diffusion coefficients of the cell wall material. Another reason might be inaccuracy of some measurements, since the experimental determination of exact diffusion coefficients is difficult, even for steady state conditions. The standard deviation s is lower for the hardwood specimens, for which all experimental values refer to only one author. This might indicate that the high standard deviation for the total set of specimens is a consequence of different measuring methods applied by the different authors. On the whole, the prediction quality of the model for steady state moisture diffusion coefficients is quite satisfactory. Considerable improvement of the model is expected from an extension to lower length scales, since wood species differ in chemical composition and therefore also in bound water diffusivity. However, this is still an active field of research. As already mentioned, the consideration of pits (in aspirated as well as in unaspirated state) would constitute a further possibility of improvement, but as long as the bound water diffusivity of the cell wall is not known exactly itself, the use of one overall diffusion coefficient for the cell wall including the pits seems reasonable.

5.5 Macroscopic regression functions based on the multiscale model

As done for thermal conductivity, regression functions were fitted to results of the multiscale homogenization model for moisture diffusivity. The used polynomial reads as

$$\dot{D}_{i} = \dot{D}_{i}^{\text{ref}} \left(a_{10,i} + a_{11,i} \,\overline{\rho} + a_{12,i} \,\overline{\rho}^{2} + a_{13,i} \frac{1}{\overline{\rho}^{3}} \right) \cdot \left(a_{20,i} + a_{21,i} \,\overline{T} + a_{22,i} \,\overline{T}^{2} + a_{23,i} \,\overline{T}^{3} + a_{24,i} \,\overline{T}^{4} \right) \cdot \left(a_{30,i} + a_{31,i} \,\overline{MC} + a_{32,i} \,\overline{MC}^{2} + a_{33,i} \,\overline{MC}^{3} + a_{34,i} \,\overline{MC}^{4} \right) \quad i \in [\mathbb{R}, \,\mathbb{T}, \,\mathbb{L}],$$
(5.43)

where $\overline{\rho}$, \overline{T} , and \overline{MC} are density, temperature, and moisture content related to reference conditions:

$$\overline{\rho} = \frac{\rho_{\text{wood}}^{\text{dry}}}{450 \,\text{kg/m}^3}, \quad \overline{T} = \frac{T}{293.15 \,\text{K}}, \quad \overline{MC} = \frac{MC}{12 \,\%}.$$
(5.44)

 \hat{D}_i^{ref} is the diffusion coefficient in direction i = R, T, L at reference conditions. An according gradient has to be specified based on mass of water per total volume of wood. The fitting coefficients a for spruce are given in Table 5.2.

5.6 Summary

In this chapter, the formulation and experimental validation of a model for moisture diffusion under steady state conditions is shown. The model revisits the morphology of wood on four different length scales that are reproduced by six homogenization steps: the wood cell structure, additional larger vessels in case of a hardwood sample, the succession of earlywood and latewood in the annual rings, and, finally, the wood rays. Thus it is possible to account for the differences in morphology of various wood species, resulting in a very good prediction quality of the model and a good correlation of calculated and corresponding measured values. This underlines the dominant influence of microstructural features such as the cell structure and the growth ring pattern on the macroscopic moisture diffusion behavior.

The presented multiscale model for the homogenization of steady state diffusion coefficients is an important special case (because of its suitability for direct validation) and an intermediate step on the way to the transient moisture diffusion model (see Chapter 9).

i	R (radial)	T (tangential)	L (longitudinal)
$\acute{D}_i^{\rm ref}$	$1.599{ imes}10^{-11}$	1.886×10^{-11}	3.320×10^{-10}
$a_{10,i}$	0.79964	1.83956	1.81373
$a_{11,i}$	-0.00613	-0.21138	-0.75624
$a_{12,i}$	-0.10923	-0.49070	-0.00787
$a_{13,i}$	0.31421	-0.13778	-0.04962
$a_{20,i}$	4401.98	4178.56	11244.7
$a_{21,i}$	-17643.3	-16783.2	-43901.4
$a_{22,i}$	26607.3	25367.3	64336.4
$a_{23,i}$	-17908.8	-17115.1	-41970.5
$a_{24,i}$	4543.81	4353.44	10291.7
$a_{30,i}$	0.09338	-0.10869	-4.14141
$a_{31,i}$	0.69667	2.13629	31.6792
$a_{32,i}$	0.35840	-3.51368	-57.8508
$a_{33,i}$	0.38874	4.57444	41.0617
$a_{34,i}$	-0.17671	-1.66885	-10.2242

Table 5.2: Reference values $\hat{D}_i^{\text{ref}} [\text{m}^2/\text{s}]$ and coefficients a_i for directions i = R, T, L, used in Eq. (5.43) for spruce clear wood, calculated based on results of the multiscale homogenization model.

5.7 Appendix A: Numerical investigation of the influence of pits

In a short numerical study the influence of pits on diffusive moisture transport was investigated. For this purpose, the effective moisture fluxes through an undistorted cell wall, a closed bordered pit, and an open bordered pit were calculated using the finite element program ABAQUS. As for material properties, the following values were used in the calculation:

air:	diffusivity $2.5 \times 10^7 \mu m^2/s$
	solubility $1.75 \times 10^{-17} \mathrm{g/\mu m^3}$
cell wall material:	diffusivity $2\mu\mathrm{m}^2/s$
	solubility $4.60 \times 10^{-13} \text{ g/}\mu\text{m}^3$

The geometries of the three investigated situations are given in Fig. 5.3, the dimensions were suitably chosen based on the photograph of the cross-section of a bordered pit. For convenience, perfect radial symmetry of the pit was assumed, therefore axisymmetric elements could be used in the calculation. By applying different concentrations to top and bottom of the model steady state conditions were gained.

The results of the examination are given in Table 5.3. The average diffusive moisture flux is almost three times higher through a closed pit than through an undistorted cell wall, and – as could be expected – more than 17 times higher through an open pit. It can be seen that, even if a pit is closed, it will clearly affect the transport behavior of water in wood.



Figure 5.3: Model representation of (a) an undistorted cell wall, (b) a closed pit, and (c) an open pit. In (d) the according microscopical image is shown [25]. The dash-dotted lines denote the middle axes of the axisymmetric models.

Table 5.3: Numerical results for the effective flux.

	undistorted cell wall	closed pit	open pit
Flux $\mathbf{J} [g/(\mu m^2 s)]$ Relation	3.786×10^{-13} 100 %	$\frac{1.087 \times 10^{-12}}{287 \%}$	$\frac{6.567 \times 10^{-12}}{1735 \%}$

5.8 Appendix B: Steady state moisture diffusivity measurements

Table 5.4: Experimental set IIa: Diffusion coefficients of wood samples, with corresponding density, moisture content and temperature

No.	Species (as reported)	Direction	n <i>MC</i> [1]	T[K]	$\begin{array}{c} \rho_{\rm wood}^{\rm dry} \\ \left[{\rm g/cm}^3\right] \end{array}$	$\stackrel{\circ}{D}^{\mathrm{exp}}_{\mathrm{wood}}_{\mathrm{[m^2/s]}}$	
1	Spruce	R	0.055	313.15	0.404	$1.06 \cdot 10^{-10}$	[55]
2	Spruce	R	0.067	313.15	0.404	$1.22 \cdot 10^{-10}$	[55]
3	Spruce	R	0.071	313.15	0.404	$1.28 \cdot 10^{-10}$	[55]
4	Spruce	R	0.083	313.15	0.404	$1.58 \cdot 10^{-10}$	[55]
5	Spruce	R	0.087	313.15	0.404	$1.56 \cdot 10^{-10}$	[55]
6	Spruce	R	0.089	313.15	0.404	$1.67 \cdot 10^{-10}$	[55]
$\overline{7}$	Spruce	R	0.091	313.15	0.404	$1.50 \cdot 10^{-10}$	[55]
8	Spruce	R	0.094	313.15	0.404	$1.78 \cdot 10^{-10}$	[55]
9	Spruce	R	0.101	313.15	0.404	$1.97 \cdot 10^{-10}$	[55]
10	Spruce	R	0.107	313.15	0.404	$1.72 \cdot 10^{-10}$	[55]
11	Spruce	R	0.117	313.15	0.404	$1.89 \cdot 10^{-10}$	[55]
12	Spruce	R	0.124	313.15	0.404	$1.86 \cdot 10^{-10}$	[55]
					Continu	ed on next p	age

		Table 5.4 –	- continue	ed from	previous	page		
No.	Species		Direction	n <i>MC</i>	T	$\rho_{\rm mag}^{\rm dry}$	D^{exp}_{max}	
	(as reported)			[1]	[K]	$\left[g/cm^{3} \right]$	$[m^2/s]$	
13	Spruce		В	0 134	313 15	0.404	$2.22 \cdot 10^{-10}$	[55]
14	Spruce		R.	0.138	313.15	0.404	$2.47 \cdot 10^{-10}$	[55]
15	Spruce		R	0.141	313.15	0.404	$2.42 \cdot 10^{-10}$	[55]
16	Spruce		R	0.151	313 15	0.404	2.12 10 $2.61.10^{-10}$	[55]
17	Spruce		R	0.101	313.15 313.15	0.404	2.01^{10} 2.86.10 ⁻¹⁰	[55]
18	Spruce		R	0.100 0.167	313.15	0.404	$2.80 \cdot 10$ $2.83 \cdot 10^{-10}$	[55]
10	Spruce		R	0.107	313.15	0.404	$3 19.10^{-10}$	[55]
20	Spruce		R	0.109	313.15	0.404	$3.06 \cdot 10^{-10}$	[55]
-0 91	Spruce		D	0.199	212 15	0.404	$3.33 10^{-10}$	[55]
21 99	Spruce		n D	0.102 0.102	212.15	0.404	3.33.10 $3.47.10^{-10}$	[55]
22 93	Spruce		n D	0.193 0.207	212.15	0.404	3.47.10 $3.61.10^{-10}$	[55]
20 24	Spruce		R	0.207 0.222	313.15 313.15	0.404	$4.00.10^{-10}$	[55]
$\frac{24}{25}$	Spruce		R	0.222 0.227	313.15 313.15	0.404	4.00.10 $4.17.10^{-10}$	[55]
20	Spruce		л D	0.221	919.15	0.404	4.17.10-10	[00]
20	Spruce		К D	0.240	313.15 212.15	0.404	$4.1(\cdot 10^{-10})$	[55]
21	Spruce		К D	0.255	313.10 212.15	0.404	$5.03 \cdot 10^{-10}$	[00]
28	Spruce		К D	0.274	313.15 212.15	0.404	$5.97 \cdot 10^{-10}$	[55]
29	Spruce		К D	0.285	313.10 222.15	0.404	$0.22 \cdot 10^{-10}$	[55]
30	Spruce		ĸ	0.030	333.15	0.404	2.00.10	[00]
31	Spruce		R	0.042	333.15	0.404	$2.36 \cdot 10^{-10}$	[55]
32	Spruce		R	0.044	333.15	0.404	$2.31 \cdot 10^{-10}$	[55]
33	Spruce		R	0.049	333.15	0.404	$2.72 \cdot 10^{-10}$	[55]
34	Spruce		R	0.055	333.15	0.404	$2.89 \cdot 10^{-10}$	[55]
35	Spruce		R	0.062	333.15	0.404	$3.28 \cdot 10^{-10}$	[55]
36	Spruce		R	0.063	333.15	0.404	$2.75 \cdot 10^{-10}$	[55]
37	Spruce		R	0.068	333.15	0.404	$3.33 \cdot 10^{-10}$	[55]
38	Spruce		R	0.069	333.15	0.404	$3.58 \cdot 10^{-10}$	[55]
39	Spruce		R	0.074	333.15	0.404	$3.50 \cdot 10^{-10}$	[55]
40	Spruce		R	0.079	333.15	0.404	$3.25 \cdot 10^{-10}$	[55]
41	Spruce		R	0.084	333.15	0.404	$3.94 \cdot 10^{-10}$	[55]
42	Spruce		R	0.087	333.15	0.404	$3.81 \cdot 10^{-10}$	[55]
43	Spruce		R	0.092	333.15	0.404	$4.36 \cdot 10^{-10}$	[55]
44	Spruce		R	0.096	333.15	0.404	$4.06 \cdot 10^{-10}$	[55]
45	Spruce		R	0.103	333.15	0.404	$5.11 \cdot 10^{-10}$	[55]
46	Spruce		R	0.106	333.15	0.404	$4.94 \cdot 10^{-10}$	[55]
47	Spruce		R	0.114	333.15	0.404	$4.94 \cdot 10^{-10}$	[55]
48	Spruce		R	0.120	333.15	0.404	$5.11 \cdot 10^{-10}$	[55]
49	Spruce		R	0.128	333.15	0.404	$5.86 \cdot 10^{-10}$	[55]
50	Spruce		R	0.135	333.15	0.404	$6.00 \cdot 10^{-10}$	[55]
51	Spruce		R	0.157	333.15	0.404	$6.39 \cdot 10^{-10}$	[55]
52	Spruce		R	0.164	333.15	0.404	$6.72 \cdot 10^{-10}$	[55]
53	Spruce		R	0.173	333.15	0.404	$7.56 \cdot 10^{-10}$	[55]
54	Spruce		R	0.176	333.15	0.404	$7.11 \cdot 10^{-10}$	[55]
						Continu	ied on next p	age

		Table 5.4 -	- continue	ed from	previous	page		
No.	Species		Direction	n <i>MC</i>	T	$\rho_{\rm wood}^{\rm dry}$	\hat{D}_{wood}^{exp}	
	(as reported)			[1]	[K]	$\left[\mathrm{g/cm}^3\right]$	$\left[\mathrm{m}^2/\mathrm{s}\right]$	
55	Spruce		R	0.191	333.15	0.404	$7.67 \cdot 10^{-10}$	[55]
56	Spruce		R	0.209	333.15	0.404	$8.19 \cdot 10^{-10}$	[55]
57	Spruce		R	0.221	333.15	0.404	$9.33 \cdot 10^{-10}$	[55]
58	Spruce		R	0.237	333.15	0.404	$1.09 \cdot 10^{-9}$	[55]
59	Spruce		R	0.247	333.15	0.404	$1.08 \cdot 10^{-9}$	[55]
60	Spruce		R	0.260	333.15	0.404	$1.16 \cdot 10^{-9}$	[55]
61	Spruce		R	0.270	333.15	0.404	$1.28 \cdot 10^{-9}$	[55]
62	Spruce		R	0.028	353.15	0.404	$3.97 \cdot 10^{-10}$	[55]
63	Spruce		R	0.036	353.15	0.404	$3.78 \cdot 10^{-10}$	[55]
64	Spruce		R	0.040	353.15	0.404	$4.86 \cdot 10^{-10}$	[55]
65	Spruce		R	0.048	353.15	0.404	$5.33 \cdot 10^{-10}$	[55]
66	Spruce		R	0.049	353.15	0.404	$4.64 \cdot 10^{-10}$	[55]
67	Spruce		R	0.055	353.15	0.404	$5.22 \cdot 10^{-10}$	[55]
68	Spruce		R	0.057	353.15	0.404	$6.00 \cdot 10^{-10}$	[55]
69	Spruce		R	0.060	353.15	0.404	$5.69 \cdot 10^{-10}$	[55]
70	Spruce		R	0.068	353.15	0.404	$7.39 \cdot 10^{-10}$	[55]
71	Spruce		R	0.069	353.15	0.404	$6.36 \cdot 10^{-10}$	[55]
72	Spruce		R	0.070	353.15	0.404	$6.72 \cdot 10^{-10}$	[55]
73	Spruce		R	0.079	353.15	0.404	$8.00 \cdot 10^{-10}$	[55]
74	Spruce		R	0.080	353.15	0.404	$7.33 \cdot 10^{-10}$	[55]
75	Spruce		R	0.087	353.15	0.404	$8.19 \cdot 10^{-10}$	[55]
76	Spruce		R	0.089	353.15	0.404	$8.75 \cdot 10^{-10}$	[55]
77	Spruce		R	0.100	353.15	0.404	$9.72 \cdot 10^{-10}$	[55]
78	Spruce		R	0.100	353.15	0.404	$9.22 \cdot 10^{-10}$	[55]
79	Spruce		R	0.110	353.15	0.404	$1.02 \cdot 10^{-9}$	[55]
80	Spruce		R	0.121	353.15	0.404	$1.22 \cdot 10^{-9}$	[55]
81	Spruce		R	0.124	353.15	0.404	$1.21 \cdot 10^{-9}$	[55]
82	Spruce		R	0.144	353.15	0.404	$1.43 \cdot 10^{-9}$	[55]
83	Spruce		R	0.154	353.15	0.404	$1.48 \cdot 10^{-9}$	[55]
84	Spruce		R	0.157	353.15	0.404	$1.54 \cdot 10^{-9}$	[55]
85	Spruce		R	0.184	353.15	0.404	$1.83 \cdot 10^{-9}$	[55]
86	Spruce		R	0.200	353.15	0.404	$2.08 \cdot 10^{-9}$	[55]
87	Spruce		R	0.203	353.15	0.404	$2.10 \cdot 10^{-9}$	[55]
88	Spruce		R	0.235	353.15	0.404	$2.67 \cdot 10^{-9}$	[55]
89	Spruce		R	0.021	373.15	0.404	$8.44 \cdot 10^{-10}$	[55]
90	Spruce		R	0.026	373.15	0.404	$9.97 \cdot 10^{-10}$	[55]
91	Spruce		R	0.031	373.15	0.404	$1.56 \cdot 10^{-9}$	[55]
92	Spruce		R	0.033	373.15	0.404	$1.14 \cdot 10^{-9}$	[55]
93	Spruce		R	0.041	373.15	0.404	$1.35 \cdot 10^{-9}$	[55]
94	Spruce		R	0.042	373.15	0.404	$1.35 \cdot 10^{-9}$	[55]
95	Spruce		R	0.045	373.15	0.404	$1.60 \cdot 10^{-9}$	[55]
96	Spruce		R	0.048	373.15	0.404	$1.34 \cdot 10^{-9}$	[55]

5.8 Appendix B: Steady state moisture diffusivity measurements

	Table 5.4 -	- continue	d from	previous	page		
No.	Species	Direction	n MC	T	$\rho^{\rm dry}$	D^{exp}	
	(as reported)		[1]	[K]	$\left[g/cm^{3} \right]$	$\left[m^2/s \right]$	
07		D	0.050	272.15		$2.06.10^{-9}$	[55]
97	Spruce	n B	0.050	373.15	0.404	2.00.10 1 60.10 ⁻⁹	[55]
90	Spruce	R	0.053	373.10 373.15	0.404	1.09.10 $1.41.10^{-9}$	[55]
100	Spruce	R	0.055	373.10 373.15	0.404	$2.01.10^{-9}$	[55]
100	Spruce	n D	0.000	979.15	0.404	2.01^{-10}	[00]
101	Spruce	K D	0.061	373.15	0.404	$1.79 \cdot 10^{-9}$	[55]
102	Spruce	K D	0.065	373.15 272.15	0.404	$2.32 \cdot 10^{-9}$	[55]
103	Spruce	К D	0.005	373.10 272.15	0.404	$1.74 \cdot 10^{\circ}$	[55]
104	Spruce	К D	0.070	373.10 272.15	0.404	$2.52 \cdot 10^{-9}$	[50]
105	Spruce	n	0.074	373.13	0.404	2.24.10	[00]
106	Spruce	R	0.078	373.15	0.404	$2.57 \cdot 10^{-9}$	[55]
107	Spruce	R	0.090	373.15	0.404	$2.38 \cdot 10^{-9}$	[55]
108	Spruce	R	0.097	373.15	0.404	$2.46 \cdot 10^{-9}$	[55]
109	Spruce	R	0.101	373.15	0.404	$2.32 \cdot 10^{-9}$	[55]
110	Spruce	R	0.112	373.15	0.404	$3.12 \cdot 10^{-9}$	[55]
111	Spruce	R	0.115	373.15	0.404	$2.36 \cdot 10^{-9}$	[55]
112	Spruce	R	0.121	373.15	0.404	$2.81 \cdot 10^{-9}$	[55]
113	Spruce	R	0.131	373.15	0.404	$2.66 \cdot 10^{-9}$	[55]
114	Spruce	R	0.143	373.15	0.404	$3.43 \cdot 10^{-9}$	[55]
115	Spruce	R	0.153	373.15	0.404	$2.98 \cdot 10^{-9}$	[55]
116	Spruce	R	0.167	373.15	0.404	$4.34 \cdot 10^{-9}$	[55]
117	Spruce	R	0.170	373.15	0.404	$2.83 \cdot 10^{-9}$	[55]
118	Spruce	R	0.177	373.15	0.404	$3.87 \cdot 10^{-9}$	[55]
119	Spruce	R	0.197	373.15	0.404	$4.71 \cdot 10^{-9}$	[55]
120	Spruce	R	0.198	373.15	0.404	$4.10 \cdot 10^{-9}$	[55]
121	Spruce	R	0.209	373.15	0.404	$5.65 \cdot 10^{-9}$	[55]
122	Norway spruce heartwood	T	0.150	333.15	0.377	$8.54 \cdot 10^{-10}$	[94]
123	Norway spruce heartwood	T	0.150	333.15	0.433	$7.36 \cdot 10^{-10}$	[94]
124	Norway spruce heartwood	Т	0.150	333.15	0.431	$6.86 \cdot 10^{-10}$	[94]
125	Norway spruce heartwood	Т	0.150	333.15	0.432	$6.71 \cdot 10^{-10}$	[94]
126	Norway spruce heartwood	Т	0 150	333 15	0.557	$5.07 \cdot 10^{-10}$	[94]
$120 \\ 127$	Norway spruce heartwood	T	0.150	333 15	0.549	$4.24 \cdot 10^{-10}$	[94]
128	Norway spruce sapwood	Ť	0.150	333 15	0.398	$7.42 \cdot 10^{-10}$	[94]
120	Norway spruce sapwood	T	0.150	333.15	0.000	7.42 10 $7.95.10^{-10}$	[04]
130	Norway spruce sapwood	T	0.150	333 15	0.400	$7.50 \ 10^{-10}$	[94]
101	Norway spruce sapwood	T	0.150	222.1E	0.110	6 19 10-10	[0 1]
131	Norway spruce sapwood		0.150	333.10 222.15	0.441	$0.18 \cdot 10^{-10}$	[94]
152 199	Norway spruce sapwood	т Т	0.150	əəə.15 999 1≝	0.433	$0.07 \cdot 10^{-10}$	[94]
100 104	Secta pine besitive a	т Т	0.150	ააა.1ე ეეე 1≝	0.078	$3.01 \cdot 10^{-10}$	[94]
154 195	Scots pine heartwood	т Т	0.150	ううう.15 222 1 m	0.507	$4.11 \cdot 10^{-10}$	[94]
120	Scots pine neartwood	1	0.100	əəə.1ə	0.550	4.30.10	[94]
136	Scots pine heartwood	Т	0.150	333.15	0.577	$3.36 \cdot 10^{-10}$	[94]
137	Scots pine heartwood	Т	0.150	333.15	0.583	$3.77 \cdot 10^{-10}$	[94]
138	Scots pine heartwood	Τ	0.150	333.15	0.583	$3.71 \cdot 10^{-10}$	[94]

	Table 3.4 – continued from previous page						
No. Spe	ecies	Directio	n <i>MC</i>	T	$\rho_{\text{wood}}^{\text{ury}}$	$D_{\text{wood}}^{\text{exp}}$	
(as	reported)		[1]	[K]	$[g/cm^3]$	$[m^2/s]$	
139 Sco	ts pine heartwood	Т	0.150	333.15	0.633	$3.08 \cdot 10^{-10}$	[94]
140 Scc	ots pine sapwood	Т	0.150	333.15	0.553	$5.36 \cdot 10^{-10}$	[94]
141 Scc	ts pine sapwood	Т	0.150	333.15	0.553	$5.09 \cdot 10^{-10}$	[94]
142 Scc	ts pine sapwood	Т	0.150	333.15	0.558	$4.92 \cdot 10^{-10}$	[94]
143 Sco	ts pine sapwood	Т	0.150	333.15	0.565	$4.89 \cdot 10^{-10}$	[94]
144 Scc	ots pine sapwood	Т	0.150	333.15	0.581	$4.88 \cdot 10^{-10}$	[94]
145 Scc	ts pine sapwood	Т	0.150	333.15	0.650	$4.12 \cdot 10^{-10}$	[94]
146 Yel	low poplar desorp.	Т	0.072	313.15	0.449	$9.00 \cdot 10^{-11}$	[11]
147 Yel	low poplar desorp.	Т	0.072	313.15	0.450	$8.80 \cdot 10^{-11}$	[11]
148 Yel	low poplar desorp.	Т	0.094	313.15	0.447	$1.66 \cdot 10^{-10}$	[11]
149 Yel	low poplar desorp.	Т	0.095	313.15	0.445	$1.65 \cdot 10^{-10}$	[11]
150 Yel	low poplar desorp.	Т	0.112	313.15	0.441	$2.14 \cdot 10^{-10}$	[11]
151 Yel	low poplar desorp.	Т	0.113	313.15	0.450	$2.26 \cdot 10^{-10}$	[11]
152 Yel	low poplar desorp.	Т	0.108	313.15	0.447	$1.55 \cdot 10^{-10}$	[11]
153 Yel	low poplar desorp.	Т	0.109	313.15	0.446	$1.57 \cdot 10^{-10}$	[11]
154 Yel	low poplar desorp.	Т	0.125	313.15	0.443	$2.26 \cdot 10^{-10}$	[11]
155 Yel	low poplar desorp.	Т	0.127	313.15	0.448	$2.42 \cdot 10^{-10}$	[11]
156 Yel	low poplar adsorp.	Т	0.068	313.15	0.449	$1.46 \cdot 10^{-10}$	[11]
157 Yel	low poplar adsorp.	Т	0.067	313.15	0.450	$1.30 \cdot 10^{-10}$	[11]
158 Yel	low poplar adsorp.	Т	0.085	313.15	0.447	$1.58 \cdot 10^{-10}$	[11]
159 Yel	low poplar adsorp.	Т	0.086	313.15	0.445	$1.54 \cdot 10^{-10}$	[11]
160 Yel	low poplar adsorp.	Т	0.101	313.15	0.441	$1.84 \cdot 10^{-10}$	[11]
161 Yel	low poplar adsorp.	Т	0.103	313.15	0.450	$1.71 \cdot 10^{-10}$	[11]
162 Yel	low poplar adsorp.	Т	0.101	313.15	0.447	$1.80 \cdot 10^{-10}$	[11]
163 Yel	low poplar adsorp.	Т	0.103	313.15	0.446	$1.82 \cdot 10^{-10}$	[11]
164 Yel	low poplar adsorp.	Т	0.116	313.15	0.443	$1.86 \cdot 10^{-10}$	[11]
165 Yel	low poplar adsorp.	Т	0.119	313.15	0.448	$2.04 \cdot 10^{-10}$	[11]
166 Yel	low poplar adsorp.	Т	0.145	313.15	0.450	$2.16 \cdot 10^{-10}$	[11]
167 Yel	low poplar adsorp.	Т	0.149	313.15	0.444	$2.22 \cdot 10^{-10}$	[11]
168 We	stern fir	R	0.060	303.15	0.360	$9.22 \cdot 10^{-11}$	[10]
169 We	stern fir	R	0.080	303.15	0.360	$1.11 \cdot 10^{-10}$	[10]
170 We	stern fir	R	0.100	303.15	0.360	$1.30 \cdot 10^{-10}$	[10]
171 We	stern fir	R	0.120	303.15	0.360	$1.48 \cdot 10^{-10}$	[10]
172 We	stern fir	R	0.140	303.15	0.360	$1.67 \cdot 10^{-10}$	[10]
173 We	stern fir	R	0.050	313.15	0.360	$9.60 \cdot 10^{-11}$	[10]
174 We	stern fir	R	0.060	313.15	0.360	$1.08 \cdot 10^{-10}$	[10]
175 We	stern fir	R	0.080	313.15	0.360	$1.60 \cdot 10^{-10}$	[10]
176 We	stern fir	R	0.100	313.15	0.360	$2.12 \cdot 10^{-10}$	[10]
177 We	stern fir	R	0.120	313.15	0.360	$2.66 \cdot 10^{-10}$	[10]
178 We	stern fir	R	0.140	313.15	0.360	$3.18 \cdot 10^{-10}$	[10]
179 We	stern fir	R	0.150	313.15	0.360	$3.24 \cdot 10^{-10}$	[10]
			0.000	000.15	0.000	1 0 10	[~]

Table 5.4 – continued from previous page

Table 5.4 – continued from previous page							
No.	Species (as reported)	Direct	ion <i>MC</i> [1]	T[K]	$ ho_{ m wood}^{ m dry} \left[{ m g/cm}^3 ight]$	$\stackrel{{ m \acute{D}}_{ m wood}}{\left[{ m m}^2/{ m s} ight]}$	
181	Western fir	R	0.080	323.15	0.360	$2.45 \cdot 10^{-10}$	[10]
182	Western fir	R	0.100	323.15	0.360	$3.22 \cdot 10^{-10}$	[10]
183	Western fir	R	0.120	323.15	0.360	$4.00 \cdot 10^{-10}$	[10]
184	Western fir	R	0.140	323.15	0.360	$4.76 \cdot 10^{-10}$	[10]
185	Western fir	R	0.050	333.15	0.360	$2.10 \cdot 10^{-10}$	[10]
186	Western fir	R	0.060	333.15	0.360	$2.36 \cdot 10^{-10}$	[10]
187	Western fir	R	0.080	333.15	0.360	$4.01 \cdot 10^{-10}$	[10]
188	Western fir	R	0.100	333.15	0.360	$5.74 \cdot 10^{-10}$	[10]
189	Western fir	R	0.120	333.15	0.360	$7.38 \cdot 10^{-10}$	[10]
190	Western fir	R	0.150	333.15	0.360	$9.30 \cdot 10^{-10}$	[10]

Chapter 6

Multiscale model for viscoelasticity of softwood

This chapter covers the development and validation of a multiscale homogenization model for linear viscoelastic properties (see footnote on page 27) of wood. Starting point is again the intrinsic structural hierarchy of wood, which is accounted for by several homogenization steps. Using the correspondence principle, an existing homogenization model for the prediction of elastic properties of wood is adapted herein for upscaling of viscoelastic characteristics. Accordingly, self-consistent, Mori-Tanaka, and unit-cell-based techniques are employed, leading to pointwise defined tensorial creep and relaxation functions in the Laplace-Carson domain. Subsequently, these functions are back-transformed into the time domain by means of the Gaver-Stehfest algorithm. With this procedure the orthotropic macroscopic creep behavior of wood can be derived from the isotropic creep behavior in shear of the lignin-hemicellulose phase. A comparison of model predictions for viscoelastic properties of softwood with corresponding experimentally derived values yields very promising results and confirms the principal suitability of the model.

6.1 Introduction

Wood is a viscoelastic material [69]. It shows an orthotropic creep and relaxation behavior, where the principal material directions are oriented along the stem axis (longitudinal direction L) and in the transverse plane perpendicular and parallel to the growth rings (radial and tangential directions R and T). For moderate load levels the viscoelastic behavior of wood can be suitably described by the linear viscoelastic theory [91]. The stress level at which non-linear viscoelastic effects start to evolve depends on the wood species, temperature, moisture content, and the type of loading (tension, compression, bending, etc.) and is usually given as a fraction of the rupture stress. According to Schniewind [91], the limit of linear behavior can range from 36 to 84 % of the static strength. The model presented in the following is formulated for linear viscoelastic behavior and, thus, is only applicable below this limit stress.

The time-dependent behavior of wood is very sensitive to moisture content [51]. High levels of moisture content implicate a lowered stiffness and an increased viscosity of wood [91], since water acts as plasticizer. Furthermore, a variable moisture content history results in so-called mechano-sorptive creep. This effect is not considered in this thesis. Rather, it focuses on time-dependent effects at constant climatic conditions for which a corresponding multiscale modeling approach is presented.

Due to the diversified microstructure of wood (see Chapter 2), involving for example the longitudinally aligned honeycomb-type cell structure, it exhibits a strongly orthotropic material behavior on the macroscale. Similar to linear elastic orthotropy with nine independent material properties, nine independent creep functions are necessary to describe the linear viscoelastic response of wood. These functions can be represented either mathematically by regression functions or by means of rheological models consisting of combinations of springs and dashpots that are arranged either in series or in parallel, see Fig. 6.1. Since these are phenomenological approaches, the unknown model parameters have to be determined by means of curve fitting methods from experimental results.

The simplest models for the description of time-dependent behavior are the Maxwell model (spring and linear dashpot in series) and the Kelvin Voigt model (spring and linear dashpot in parallel), see Fig. 6.1. Their combination in series, resulting in the Burgers model, provides a suitable description of the rheological behavior of wood and is frequently applied (see, e.g. [29], [30], [54], [58]). In general, this type of model is only applicable to a limited time range, namely either to short-term or to long-term behavior). To overcome this limitation, generalized models like the generalized Maxwell model or the generalized Kelvin Voigt model were developed (see, e.g. [39], [41]). These consist of a multitude of Maxwell or Kelvin Voigt models arranged in parallel, each with a different characteristic time. The large number of parameters included in these models enables to adjust the model response to measured creep curves. The main advantage of these generalized models is their rather easy implementation in finite element codes for numerical simulations [108]. However, a large number of parameters complicates relating the observed effects and the single rheological elements to underlying physical phenomenons and furthermore requires large sets of experimental data for their identification.

A very promising model for the time-dependent behavior of wood in the cross-grain directions is the power law model specified in Fig. 6.1(e) (see, e.g., [69, 92, 50]). This model consists of a linear spring connected in series with a nonlinear, so-called parabolic or fractional dashpot.

As for macroscopic transport properties, the wide variability of viscoelastic material properties stems from differences in morphology and chemical composition on lower length scales. This motivates to follow the same homogenization strategy as presented in Chapter 4 and 5. Along these lines, the model for viscoelastic properties of wood builds up on the multiscale homogenization model for wood stiffness [44, 45, 46, 4].



Figure 6.1: Rheological models, model parameters for the description of deviatoric creep, creep compliance J(t), and Laplace-Carson transform $J^*(s)$: (a) Maxwell model [3]; (b) Kelvin Voigt model [3]; (c) three-parameter model [3]; (d) fractional dashpot; (e) power-law model [3]; (f) fractional Zener model [74]

6.2 Upscaling of mechanical properties

As mentioned in the introduction, a combination of continuum micromechanics and the unit cell method turned out suitable to represent the morphology of wood across the different length scales for upscaling of elastic properties of wood [44, 45, 46, 4], see Fig. 6.2. Using the Laplace-Carson transform and the correspondence principle, this model will serve as basis for the upscaling of viscoelastic properties in this paper.

6.2.1 Homogenization of elastic properties of randomly organized materials: Continuum micromechanics

As done for transport properties, continuum micromechanics may be used as an analytical technique for determination of the effective mechanical properties of a macrohomogeneous but micro-heterogeneous material. Again the material is described in a statistical manner by a so-called representative volume element (RVE) composed of homogeneous subdomains, so-called material phases r, with known properties such as volume fraction f_r and a phase elasticity law reading as

$$\boldsymbol{\sigma}_r = \mathbb{C}_r : \boldsymbol{\varepsilon}_r, \tag{6.1}$$

where \mathbb{C}_r is the stiffness tensor, and σ_r and ε_r are the stress and strain within phase r. The effective (homogenized) stiffness \mathbb{C}^{hom} of the overall material, i.e. the relation between homogeneous deformations acting on the boundary of the RVE and resulting (average) stresses in the RVE, can be derived from Eshelby-Laws-type matrix-inclusion problems [24, 59] as

$$\mathbb{C}^{\text{hom}} = \sum_{r} f_{r} \mathbb{C}_{r} : \left[\mathbb{I} + \mathbb{P}_{r}^{0} : (\mathbb{C}_{r} - \mathbb{C}^{0}) \right]^{-1} : \left\{ \sum_{s} f_{s} \left[\mathbb{I} + \mathbb{P}_{s}^{0} : (\mathbb{C}_{s} - \mathbb{C}^{0}) \right]^{-1} \right\}^{-1}, \quad (6.2)$$

where I is the fourth order unity tensor, and \mathbb{P}_r^0 is the Hill tensor accounting for the shape of the inclusion embedded in a matrix with stiffness \mathbb{C}^0 [113, 24, 40]. The two sums are taken over all phases in the RVE.

6.2.2 Homogenization of elastic properties of periodically organized materials: Unit cell method

The unit cell method [7, 68] is used to determine the effective mechanical behavior of a micro-heterogeneous material through approximating the real microstructure by a periodic one and by studying the mechanical behavior of the basic repetitive unit (the *unit cell*). Subjecting the unit cell to periodic deformations at its boundaries (which are compatible with the macroscopic strains) allows for determination of the resulting inhomogeneous stress and strain fields in the microstructure. Depending on the complexity of the microstructure, these fields can be determined analytically [9, 46] or numerically, e.g. by means of the finite element method [8, 53]. The homogenized mechanical behavior is estimated from evaluating the average values of the periodic micro-stress field in the unit cell in relation to the macroscopic strains acting on the boundary of the unit cell.

6.2.3 Homogenization of viscoelastic material properties: Elastic-viscoelastic correspondence principle

In general, viscoelasticity is the behavior of materials showing an accumulation of strains under constant stress (creep) and/or a reduction of stress under constant strain (relaxation). The constitutive behavior of a viscoelastic material phase r for a specific strain history $\varepsilon_r(t)$ can be expressed by

$$\boldsymbol{\sigma}_{r}(t) = \int_{0}^{t} \mathbb{R}_{r}(t-\tau) : \dot{\boldsymbol{\varepsilon}}_{r}(\tau) \,\mathrm{d}\tau, \tag{6.3}$$

where $\dot{\varepsilon}_r$ is the time derivative of the strain tensor, \mathbb{R}_r is the fourth order relaxation tensor, t is the time, and τ is an integration variable marking the time when $\dot{\varepsilon}$ was imposed. Thereby, $\mathbb{R}_r(t = \tau)$ refers to instantaneous elasticity, while $\mathbb{R}_r(t > \tau)$ refers to viscoelastic deformations. The special case of constant $\mathbb{R}_r(t)$ refers to pure elasticity, i.e. $\mathbb{R}_r(t) = \mathbb{C}_r$, with \mathbb{C}_r being the fourth-order elastic stiffness tensor of phase r. Alternatively, the local viscoelastic material behavior of phase r can be characterized by the creep function $\mathbb{D}_r(t)$, relating microscopic strains and stresses by

$$\boldsymbol{\varepsilon}_{r}(t) = \int_{0}^{t} \mathbb{D}_{r}(t-\tau) : \dot{\boldsymbol{\sigma}}_{r}(\tau) \,\mathrm{d}\tau.$$
(6.4)

In Eqs. (6.3) and (6.4) the Boltzmann superposition principle is used, which states that – given a linear relation between stresses and strains – the combined effect of several loads is the sum of the effects of the individual loads. By applying a Laplace-Carson (LC) transform, the convolution-type constitutive relations Eqs. (6.3) and (6.4) in the time-domain become standard algebraic equations in the Laplace-Carson domain. This transform is defined as [14]

$$f^*(s) = \mathcal{LC}[f(t)] = s \mathcal{L}[f(t)] = s \hat{f}(s) = s \int_0^\infty f(t) e^{-st} dt, \qquad (6.5)$$

where $f^*(s)$ is the LC transform of the time-dependent function f(t), s is the complex variable in the LC domain, and $\hat{f}(s)$ is the Laplace transform of f(t). Application of Eq. (6.5) to the relaxation law [Eq. (6.3)] and to the creep law [Eq. (6.4)] yields the according algebraic constitutive equations [36]

$$\boldsymbol{\sigma}_r^*(s) = \mathbb{R}_r^*(s) : \boldsymbol{\varepsilon}_r^*(s) \tag{6.6}$$

and

$$\boldsymbol{\varepsilon}_r^*(s) = \mathbb{D}_r^*(s) : \boldsymbol{\sigma}_r^*(s). \tag{6.7}$$

The analogy between Eq. (6.6) and the linear-elastic constitutive law [Eq. (6.1)] is the basis for the solution of viscoelastic problems by means of the correspondence principle (see e.g. [65]). Hereby, the material parameters in the solution of the respective elastic problem are replaced by the respective LC transformed viscoelastic parameters. For example, the elastic shear compliance $1/\mu$ is replaced by the LC transformed creep-compliance function for deviatoric creep, $j_{\text{dev}}^*(s)$. With the elastic solution for the effective properties of composite materials at hand [Eq. (6.2)], the correspondence principle gives access to the macroscopic viscoelastic state equations as

$$\boldsymbol{\Sigma}^*(s) = \mathbb{R}^{\text{hom},*}(s) : \mathbf{E}^*(s), \tag{6.8}$$

with $\mathbb{R}^{\text{hom},*}(s)$ denoting the LC-transform of the homogenized macroscopic relaxation tensor. The inverse LC transform delivers the corresponding solutions in the time domain:

$$f(t) = \mathcal{L}\mathcal{C}^{-1}[f^*(s)] = \frac{1}{2i\pi} \int_{\Gamma} \frac{f^*(s)}{s} e^{pt} \,\mathrm{d}s,$$
(6.9)

where Γ is parallel to the imaginary axis having all poles of $f^*(s)$ on the left [3]. A further advantage of the LC transform is that time-independent functions remain unaffected, i.e. they are equivalent in the time-domain (f(t) = f = const) and in the Laplace Carson domain $(f^*(s) = f = \text{const})$. Application of the LC transform to purely elastic material properties therefore yields:

$$\mathbb{R}^*_{r,\text{elastic}}(s) = \mathbb{C}_{r,\text{elastic}}.$$
(6.10)

Equation (6.10) allows for combination of viscoelastic and elastic materials in a homogenization procedure.

6.3 Definition of the multiscale homogenization model

On the basis of the correspondence principle, exploiting the analogy between elastic and LC-transformed viscoelastic constitutive equations, the multiscale homogenization model derived for elasticity of softwood by Hofstetter [46] can be easily adopted to viscoelasticity (see Fig. 6.2). The resulting multistep homogenization procedure involves four RVEs at different length scales:

- an RVE of *polymer network* consisting of lignin, hemicellulose, and water;
- an RVE of *cellulose* consisting of crystalline cellulose fibrils embedded in amorphous cellulose;
- an RVE of *cell wall material* consisting of cellulose fibers surrounded by a matrix of polymer network;
- an RVE of *softwood* as porous honeycomb made up of cell wall material, where the pores are referred to as "lumens".



Figure 6.2: Four-step homogenization scheme on three hierarchical levels.

The morphological parameters and phase volume fractions of the various homogenization steps are independent of the considered material property. Therefore, densities, volume fractions, and aspect ratios of the single phases can be directly taken from the elastic model [46]. The chosen RVEs and their morphology are again a model representation of the much more complicated real structure of wood.

Compared to the homogenization approaches given in the preceding chapters, obviously a different representation is chosen. The reason is that the influence of microstructural characteristics is different with regard to the considered material property. For example, cellulose strongly influences the macroscopic mechanical behavior, therefore a more detailed representation for cellulose is chosen in step I(b). In addition, step III is adapted for a better description of the mechanical response of the cellular structure by using a unit cell approach. As for transport properties, steps IV, V, and VI in the models presented in Chapters 4 and 5 represent in detail the hollow transport routes (lumens, vessels, and rays). As for mechanical properties these steps are much less significant, therefore they were omitted. In general, simplifications on lower scales in a modeling approach can be accepted as long as they don't affect the macroscopic behavior beyond commonly accepted levels of modeling inaccuracies.

6.3.1 Step I(a): Polymer network

In step I(a) the dispersed structure of polymer network is reproduced by mixing spherical inclusions, representing the phases lignin, hemicellulose, and water. In contrast to the model of Hofstetter [44], lignin and hemicellulose are treated together as ligninhemicellulose phase, since individual viscoelastic properties of these two phases are not known yet and difficult if not impossible to access experimentally. Substituting the LCtransformed viscoelastic quantities of the phases for the corresponding elastic quantities, (e.g. $\mathbb{R}^*_{H_2Oext}(s)$ for \mathbb{C}_{H_2Oext}) in Eq. (5) in [44], yields a relation for the LC-transformed relaxation tensor $\mathbb{R}^{hom,*}_{poly}(s)$,

$$\mathbb{R}_{\text{poly}}^{\text{hom},*}(s) = \left\{ \sum_{r} \tilde{f}_{r} \mathbb{R}_{r}^{*}(s) : \left[\mathbb{I} + \mathbb{P}_{\text{sph}}^{\text{poly},*}(s) : \left(\mathbb{R}_{r}^{*}(s) - \mathbb{R}_{\text{poly}}^{\text{hom},*}(s) \right) \right]^{-1} \right\} : \left\{ \sum_{t} \tilde{f}_{t} \left[\mathbb{I} + \mathbb{P}_{\text{sph}}^{\text{poly},*}(s) : \left(\mathbb{R}_{t}^{*}(s) - \mathbb{R}_{\text{poly}}^{\text{hom},*}(s) \right) \right]^{-1} \right\}^{-1},$$

$$(6.11)$$

 $r, t \in [\text{lig}+\text{hemcel}, \text{H}_2\text{Oext}],$

with $\tilde{f}_{\text{lig+hemcel}} = \tilde{f}_{\text{hemcel}} + \tilde{f}_{\text{lig}}$ and $\tilde{f}_{\text{H}_2\text{Oext}}$ denoting the volume fractions of the ligninhemicellulose matrix and of water mixed with extractives, respectively. The LC-transformed Hill tensor $\mathbb{P}^{\text{poly},*}_{\text{sph}}(s)$ accounts for the distribution and the characteristic shape of these phases in the polymer network (see e.g. [40] for its components).

6.3.2 Step I(b): Cellulose

Step I(b) represents the structure of cellulose macrofibrils. This step is an improvement of the homogenization scheme presented in Hofstetter et al. [44], where crystalline and amorphous parts of cellulose are considered as individual phases in the cell wall (cf. Bader et al. [4]). Replacing the LC-transformed viscoelastic properties of crystalline and amorphous celluloses by the corresponding elastic properties in Eq. (32) in Bader et al. [4], the LC-transformed relaxation tensor of cellulose $\mathbb{R}^{\text{hom},*}_{\text{cel}}(s)$ reads as

$$\mathbb{R}_{cel}^{hom,*}(s) = \left\{ \hat{f}_{amocel} \mathbb{R}_{amocel}^{*}(s) + \hat{f}_{crycel} \mathbb{R}_{crycel}^{*}(s) : \left[\mathbb{I} + \mathbb{P}_{cyl}^{amocel,*}(s) : \left(\mathbb{R}_{crycel}^{*}(s) - \mathbb{R}_{amocel}^{*}(s) \right) \right]^{-1} \right\} : \left\{ \hat{f}_{amocel} \mathbb{I} + \hat{f}_{crycel} \left[\mathbb{I} + \mathbb{P}_{cyl}^{amocel,*}(s) : \left(\mathbb{R}_{crycel}^{*}(s) - \mathbb{R}_{amocel}^{*}(s) \right) \right]^{-1} \right\}^{-1}.$$

$$(6.12)$$

The components of the LC-transformed Hill tensor $\mathbb{P}^{\text{amocel},*}_{\text{cyl}}(s)$ can be derived from that specified in [4] by replacing the components of the elastic stiffness tensor by the corresponding components of the LC-transformed relaxation tensor.

6.3.3 Step II: Cell wall material

The RVE of cell wall material comprises the material phases "cellulose" with volume fraction f_{cel} and LC-transformed relaxation tensor $\mathbb{R}_{cel}^{\hom,*}(s)$ as described in the previous Subsection 6.3.2, and "polymer network" with volume fraction $f_{poly} = 1 - f_{cel}$ and LC-transformed viscoelastic behavior characterized by the LC-transformed relaxation tensor $\mathbb{R}_{poly}^{\hom,*}(s)$, see Subsection 6.3.1. According to the correspondence principle, the equations for elasticity given in [45] and for LC-transformed viscoelasticity again show the same structure. Thus, the LC-transformed relaxation tensor $\mathbb{R}_{cwm}^{\hom,*}(s)$ of the cell wall material reads as

$$\mathbb{R}_{cwm}^{hom,*}(s) = \left\{ f_{poly} \mathbb{R}_{poly}^{hom,*}(s) + \frac{1}{2\pi} \int_{0}^{2\pi} \mathbb{R}_{cel}^{*}(\varphi, \bar{\theta}, s) : \left[\mathbb{I} + \mathbb{P}_{cyl}^{poly,*}(\varphi, \bar{\theta}, s) : \left(\mathbb{R}_{cel}^{hom,*}(\varphi, \bar{\theta}, s) - \mathbb{R}_{poly}^{hom,*}(s) \right) \right]^{-1} d\varphi \right\} : \left\{ f_{poly} \mathbb{I} + f_{cel} \frac{1}{2\pi} \int_{0}^{2\pi} \left[\mathbb{I} + \mathbb{P}_{cyl}^{poly,*}(\varphi, \bar{\theta}, s) : \left(\mathbb{R}_{cel}^{hom,*}(\varphi, \bar{\theta}, s) - \mathbb{R}_{poly}^{hom,*}(s) \right) \right]^{-1} d\varphi \right\}^{-1},$$

$$\left[\mathbb{I} + \mathbb{P}_{cyl}^{poly,*}(\varphi, \bar{\theta}, s) : \left(\mathbb{R}_{cel}^{hom,*}(\varphi, \bar{\theta}, s) - \mathbb{R}_{poly}^{hom,*}(s) \right) \right]^{-1} d\varphi \right\}^{-1},$$

where $\bar{\theta}$ (identical to the average microfibril angle in the S2 layer) and φ denote the two Euler angles describing the position of the macrofibril axis in a Cartesian coordinate system. These two angles account for the helically wound arrangement of the cellulose fibers in the wood cell wall. As in the previous steps, the LC-transformed Hill tensor $\mathbb{P}_{cyl}^{poly,*}(s)$ accounts for the distribution and the characteristic shape of the cellulose phase embedded in a matrix of polymer network. A more detailed description of this homogenization step is given in [45].

6.3.4 Step III: Softwood

From a modeling point of view, the structure of softwood can be suitably approximated by a large number of identical, periodically arranged unit cells, which motivates the use of the unit cell method with periodic boundary conditions. Application of this method for estimation of elastic material properties of wood has been shown in [46]. As in the previous steps, the LC transform allows for adaptation of the elastic formulation to viscoelastic behavior. The LC-transformed relaxation tensor of softwood, $\mathbb{R}_{SW}^{\text{hom},*}(s)$, can be calculated directly based on the equations for the stiffness tensor of softwood given in Appendix C in [46] by replacing the components of the stiffness tensor of the cell wall material, $c_{\text{cwm},ijkl}$, by the corresponding components of the LC-transformed relaxation tensor of the cell wall material, $R_{\text{cwm},ijkl}^{\text{hom},*}(s)$ [Eq. 6.13].

6.4 Inversion of the Laplace-Carson transform – determination of creep and relaxation functions in the time domain

The viscoelastic material properties for softwood estimated by means of the multiscale homogenization scheme presented in the previous section are obtained in the LC domain. Corresponding solutions in the time domain can be determined through the inverse LC transformation as specified in Eq. (6.9). This inverse transform can be performed analytically only for simple rheological models, while numerical techniques are required for materials with a more complex rheological behavior, as it is the case for wood. Use of the Gaver-Stehfest algorithm [101] provides discrete values of the time-dependent functions, e.g. of relaxation tensor $\mathbb{R}^{\text{hom}}_{\text{SW}}(t)$ and creep compliance tensor $\mathbb{D}^{\text{hom}}_{\text{SW}}(t)$ of softwood, at a given time t as

$$\mathbb{R}_{SW}^{hom}(t) = \mathcal{L}\mathcal{C}^{-1}\left\{\mathbb{R}_{SW}^{hom,*}(s)\right\},\tag{6.14}$$

$$\mathbb{D}_{\mathrm{SW}}^{\mathrm{hom}}(t) = \mathcal{L}\mathcal{C}^{-1}\left\{\mathbb{D}_{\mathrm{SW}}^{\mathrm{hom},*}(s)\right\} = \mathcal{L}\mathcal{C}^{-1}\left\{\left[\mathbb{R}_{\mathrm{SW}}^{\mathrm{hom},*}(s)\right]^{-1}\right\}.$$
(6.15)

Given the orthotropic material behavior of wood, the LC-transformed creep compliance tensor $\mathbb{D}_{SW}^{\hom,*}(s)$ can be formulated in terms of nine independent viscoelastic material parameters, reading in compressed matrix notation as

$$\mathbb{D}_{\rm SW}^{\rm hom,*}(s) = \begin{bmatrix} \frac{1}{E_{\rm R}^*(s)} & -\frac{\nu_{\rm RT}^*(s)}{E_{\rm R}^*(s)} & -\frac{\nu_{\rm RL}^*(s)}{E_{\rm R}^*(s)} & 0 & 0 & 0 \\ & \frac{1}{E_{\rm T}^*(s)} & -\frac{\nu_{\rm TL}^*(s)}{E_{\rm T}^*(s)} & 0 & 0 & 0 \\ & & \frac{1}{E_{\rm T}^*(s)} & 0 & 0 & 0 \\ & & & \frac{1}{G_{\rm RT}^*(s)} & 0 & 0 \\ & & & & \frac{1}{G_{\rm TL}^*(s)} & 0 \\ & & & & & \frac{1}{G_{\rm TL}^*(s)} & 0 \\ & & & & & \frac{1}{G_{\rm LR}^*(s)} \end{bmatrix}_{\rm SW}^{\rm hom}.$$
(6.16)

In Eq. (6.16) the three LC-transformed relaxation moduli $E_{\rm R}^*(s)$, $E_{\rm L}^*(s)$, $E_{\rm L}^*(s)$, the three LC-transformed time-dependent Poisson's ratios $\nu_{\rm RT}^*(s)$, $\nu_{\rm RL}^*(s)$, $\nu_{\rm TL}^*(s)$, and the three LC-transformed time-dependent shear moduli $G_{\rm RT}^*(s)$, $G_{\rm TL}^*(s)$, $G_{\rm LR}^*(s)$ are employed as such parameters.

In order to end up with a (analytical) macroscopic rheological model and according model parameters, suitable creep-compliance functions (cf. Fig. 6.1) can be fitted to the

pointwise estimated compliance function $\mathbb{D}_{SW}^{hom}(t_i)$. For the choice of a macroscopic rheological model and, thus, of a creep compliance function, the depiction of the estimates by the multiscale model in a Cole-Cole diagram is very useful. This is detailed in Section 6.7. First, the viscoelastic input parameters are identified, and then an experimental model validation is performed.

6.5 Identification of rheological properties of the elementary components

As mentioned in the introduction, the lignin-hemicellulose phase is assumed to be the only elementary component of wood exhibiting viscoelastic material behavior. The other constituents of wood (amorphous and crystalline cellulose, water clustered with extractives) are assumed to exhibit a purely elastic behavior, leading in accordance with Eq. (6.10) to

$$\mathbb{R}_r^*(s) = \mathbb{C}_r, \quad r \in [\text{amocel, crycel, H}_2\text{Oext}], \tag{6.17}$$

with the stiffness tensors \mathbb{C}_r according to Table 6.1. As for water, two assumptions are made therein: First, viscosity of water is neglected, expressed by zero shear modulus $\mu_{\text{H}_2\text{Oext}} = 0$. Second, the model is restricted to constant moisture content, therefore the volume fraction of water is constant and independent of the mechanical stress state.

The lignin-hemicellulose phase is assumed to exhibit isotropic creep behavior at shear loading [6]. Under hydrostatic loading, the phase is assumed to behave elastically, so that the LC transform of the bulk modulus, $k_{\text{lig+hemcel}}^*(s)$, is constant and equals the mean elastic bulk modulus of this phase, $k_{\text{lig+hemcel}} = 6.40 \text{ GPa}$ (Table 6.1). This yields the following constitutive relation:

$$\mathbb{R}^*_{\text{lig+hemcel}}(s) = \left[\mathbb{D}^*_{\text{lig+hemcel}}(s)\right]^{-1} = 3k_{\text{lig+hemcel}} \mathbb{K} + 2\mu^*_{\text{lig+hemcel}}(s)\mathbb{J}, \tag{6.18}$$

where $\mu_{\text{lig+hemcel}}^*(s)$ is the LC-transformed shear modulus of the lignin-hemicellulose phase. K denotes the volumetric part of the fourth-order unity tensor with components $K_{ijkl} = 1/3\delta_{ij}\delta_{kl}$, and $\mathbb{J} = \mathbb{I} - \mathbb{K}$ the deviatoric part of the fourth order unity tensor.

Phase	Material behavior	Bulk modulus [GPa]	Shear modulus [GPa]	Source		
Amorphous cellulose Lignin + hemicellulose Water + extractives	isotropic isotropic isotropic	$k_{ m amocel} = 5.56$ $k_{ m lig+hemcel} = 6.40$ $k_{ m H_2Oext} = 2.30$	$\begin{split} \mu_{\rm amocel} &= 1.85 \\ \mu_{\rm lig+hemcel} &= 2.24 \\ \mu_{\rm H_2Oext} &= 0 \end{split}$	[18] [12, 13]		
		Stiffness tensor components C_{ijkl} [GPa]				
Crystalline cellulose	transversely isotropic	$C_{\text{crycel},1111} = 34.86$ $C_{\text{crycel},1111} = 167.79$ $C_{\text{crycel},1111} = 5.81$	$C_{\text{crycel},1122} = 0$ $C_{\text{crycel},2233} = 0$	[103]		

Table 6.1: Input data set I: Tissue-independent elastic phase properties

The viscoelastic shear behavior of typical polymers is well described by a power-law model [79], as depicted in Fig. 6.1. This model consists of a linear spring connected

in series with a nonlinear, so-called parabolic or fractional dashpot. The corresponding LC-transformed shear relaxation modulus reads as

$$\mu_{\text{lig+hemcel}}^*(s) = \left(\frac{1}{\mu_{0,\text{lig+hemcel}}} + J_{a,\text{lig+hemcel}}\frac{1}{(s\,t_a)^{\alpha_{\text{lig+hemcel}}}}\Gamma\left(1+\alpha_{\text{lig+hemcel}}\right)\right)^{-1},\tag{6.19}$$

where $\mu_{0,\text{lig+hemcel}}$ [GPa] is the instantaneous elastic shear modulus, $J_{a,\text{lig+hemcel}}$ [GPa⁻¹] is the viscous part of the creep compliance at time $t = t_a$, and $\alpha_{\text{lig+hemcel}}$ denotes the creep exponent of the lignin-hemicellulose phase. The power-law model exhibits two regimes of evolving strains provoked by constant stress: (i) an instantaneous elastic response, followed by (ii) a degrading creep response. The creep exponent α governs the creep kinetics: For $\alpha = 0$, the fractional dashpot behaves like a spring, while it resembles a linear dashpot for $\alpha = 1$. Typical values of α for polymers specified in literature range from 0.04 (cross-linked polyethylene [75]) to 0.346 (vinyl ester [79]). Due to lack of experimentally derived creep properties of lignin and hemicellulose, respectively, these two phases were treated together and calibrated by matching model predictions to results of a macroscopic normal creep experiment perpendicular to the grain reported by Schniewind [92] (board No. 267, Douglas-fir, dry density $\rho = 477 \text{ kg/m}^3$, moisture content MC = 10%). The microfibril angle was set to $\theta = 15^{\circ}$, which is a typical value for softwoods. For this specific sample, Schniewind specified the following tangential creep compliance function based on his test results (transformed to SI units):

$$J_{\rm T}^{\rm exp}(t) = 1.3268 \,{\rm GPa}^{-1} + 0.08016 \,{\rm GPa}^{-1} \left(\frac{t}{1\,{\rm min}}\right)^{0.2075}.$$
(6.20)

This relation can be represented rheologically by a power-law model (see Fig. 6.1). Using the multiscale model presented in Section 6.3 and considering the sample-specific input parameters (wood species, density, moisture content, and microfibril angle), the viscoelastic material parameters of the lignin-hemicellulose phase in Eq. (6.19) were determined such that the resulting model predictions match the creep compliance function in Eq. (6.20) as closely as possible. This yields:

$$\mu_{0,\text{lig+hemcel}} = 3.6765 \,\text{GPa},
J_{a,\text{lig+hemcel}} = 0.0104 \,\text{GPa}^{-1} \quad (t_a = 1 \,\text{s}),
\alpha_{\text{lig+hemcel}} = 0.221.$$
(6.21)

The initial elastic shear modulus μ_0 is higher than the values used for lignin and hemicellulose in the elastic model for wood (see Table 6.1). This can be appropriate, because creep starts immediately after application of a load, and therefore also the "elastic" shear modulus typically observed in quasi-static testing already comprises a viscoelastic share.

6.6 Experimental validation

The experimental validation of the developed multiscale model is based on a comparison of model predictions for given sample-specific volume fractions and morphological properties (input data set II), with corresponding experimental data, namely the remaining



Figure 6.3: Relative creep curves. The points are experimental values given by Schniewind [92], the solid lines denote the creep behavior predicted with the multi-scale model. The experimental data for normal creep in tangential direction was used to calibrate the model, what is indicated by a dash-dotted line for the according model prediction.

data given in Schniewind [92] and additional data from Lotfy [61] (experimental data set).

First the verification of the behavior of the model over a longer period is made by comparison of experimentally derived relative creep curves [92] and corresponding model predictions (Fig. 6.3). Three different types of creep compliances are considered: normal creep in longitudinal direction and transverse creep in tangential direction under a longitudinal load and shear creep for a shear load in the tangential-longitudinal plane. Points in Fig. 6.3 indicate the experimental values, lines show associated model predictions. The data for normal creep in tangential direction was used for the calibration of the model, therefore the according model prediction is labeled as dash-dotted line.

Also for the other three types of compliances, a very good correlation between model predictions and associated experimental values can be observed. This confirms the suitability of assigning the microscale origin of creep to the lignin-hemicellulose phase and is the main advantage of the model: different macroscopic creep effects both in longitudinal and in transverse direction, can be explained by only one creep law on the nanometer scale. So far, it was common to employ different formulations for creep in these two directions.

The prediction quality of the model for different samples is checked by means of the further test data published by Schniewind for samples of other densities [92] and Lotfy [61] for samples of different microfibril angle. Normal creep in longitudinal and transversal
plane are considered. A one-to-one comparison of experimental and modeling data is illustrated in Fig. 6.4, where each marker indicates one pair of creep measurement (abscissa) and corresponding model prediction (ordinate). Different markers are used to depict the different principal material directions as well as different sources. Two plots are drawn for each compliance characteristic: the initial compliance and the increase in compliance within 60 minutes for data given by Lotfy $[\Delta J_i = J_i(t = 60 \min) - J_i(t = 0)]$ and within 1000 minutes $[\Delta J_i = J_i(t = 1000 \min) - J_i(t = 0)]$ for data of Schniewind. The solid diagonal lines indicate perfect agreement of model predicted and experimental values.

As for the initial normal compliance in longitudinal direction, model predictions are suitable [cf. Fig. 6.4(a)], although the relatively wide spread in the experimental values cannot be completely reproduced by the model. This might be caused by variability of microstructural characteristics, such as MFA or chemical composition, which was not taken into account due to missing information in the references.

For the time-dependent increase in normal compliance [Fig. 6.4(b)], the wide spread of experimental values is even more pronounced, though not reproduced by the model either. Several possible reasons for this deviation can be given. For example, there are inevitable inaccuracies of the measurements. Due to the low normal compliance in longitudinal material direction and the small resulting strains, already small absolute measurement errors might affect the test results pronouncedly. Again, also the disregarded variability of microstructural characteristics in the model evaluations could contribute to deviations between experimental and predicted values. Moreover, simplifications in the model could also contribute to the observed deviations. According possible model improvements are given at the end of this section.

As for the radial and the tangential direction, both the initial normal compliances [see Fig. 6.4(c)] and their increases are quite well reproduced [see Fig. 6.4(d)]. The influence of time-dependent effects on normal compliance is much more pronounced for loads in transverse direction than for loads in longitudinal direction. This is caused by the alignment of the purely elastic macrofibrils mainly in the latter direction.

The best agreement is observed for the initial shear compliance [Fig. 6.4(e)] and its creepinduced increase [Fig. 6.4(f)]. Both comparisons show a very good prediction quality of the multiscale model for this material parameter.

As shown, the model predictions are very suitable for creep in radial and tangential direction as well as for shear creep. In these directions the choice of the lignin-hemicellulosecomplex being the origin of wood creep is reasonable. In longitudinal direction, only the initial compliance is feasibly predicted, while the additional creep compliance is underestimated. Possible reasons for this deficiency of the model are:

- The amorphous parts of the cellulose macrofibrils might exhibit (anisotropic) viscoelastic material behavior.
- In the direction of the macrofibril axis, the crystalline parts of cellulose are interrupted by paracrystalline sections [87] which might show viscoelastic material behavior.
- Hemicellulose is partly aligned in the direction of the macrofibrils [102]. Its material



Figure 6.4: Comparison of model predictions with experimental results for initial normal compliances (left column) and increases in normal compliances within 60 minutes (Lotfy) and 1000 minutes (Schniewind) [Schniewind $(\Box, +, \times)$, Lotfy (\blacksquare)]: (a) and (b) longitudinal material direction; (c) and (d) radial (+) and tangential (×) material direction; (e) and (f) radial-longitudinal (×) material direction.

behavior might therefore be anisotropic, with different creep behavior parallel and perpendicular to the fiber axis.

According model extensions would require more detailed information about the viscoelastic material behavior of the single phases, including a much higher number of material parameters especially for the case of anisotropic behavior. Since this information is not available at the moment, the presented simplified model appears justified.

6.7 Macroscopic rheological characteristics of the multiscale model

To illustrate the performance of the model and to identify possible macroscopic rheological representations, the three relaxation moduli $E_{\rm R}(t)$, $E_{\rm T}(t)$, $E_{\rm L}(t)$, the three viscoelastic Poisson's ratios $\nu_{\rm RT}(t)$, $\nu_{\rm RL}(t)$, $\nu_{\rm TL}(t)$, and the three viscoelastic shear moduli $G_{\rm RT}(t)$, $G_{\rm TL}(t)$, $G_{\rm LR}(t)$ are depicted in so-called Cole-Cole diagrams. These show the characteristics of a particular material parameter by plotting its complex part against its real part for different frequencies in the LC domain. In case of a relaxation modulus E^* , the real part E' is also called storage modulus, while the complex part E'' is called loss modulus.

Each rheological model shows a characteristic curve in the Cole-Cole diagram. For example, a Maxwell model is characterized by a semi circle with the center point on the real axis and both loss modulus and storage modulus approaching zero for low frequencies, while a Kelvin-Voigt model is represented by a vertical straight line, due to a constant storage modulus and a loss modulus tending against infinity for frequencies approaching zero.

Figure 6.5 shows the resulting curves for the aforementioned viscoelastic material parameters for spruce with a density of $\rho_{\text{wood}}^{\text{dry}} = 450 \text{ kg/m}^3$, a moisture content of MC = 10 %, and a microfibril angle of $\bar{\theta} = 15^\circ$. Two classes can be distinguished:

- For the radial and tangential relaxation moduli and the radial-tangential shear relaxation modulus, the rheological behavior can be described by a power-law model as depicted in Fig. 6.1. The associated Cole-Cole diagram shows a parabolic curve and as for the Maxwell model a loss modulus and a storage modulus of zero at low frequencies. This behavior can be explained by the continuous viscoelastic polymer network phase in the radial-tangential plane.
- For the longitudinal relaxation modulus and the viscoelastic shear moduli in the tangential-longitudinal and longitudinal-radial direction, a residual resistance also at low frequencies, i.e. for long term loads, is observed. This is a consequence of the stiff, purely elastic behavior of the macrofibrils. In the Cole-Cole diagram such a behavior is characterized by a non-zero storage modulus for low frequencies. A power law model with an additional spring in parallel, as depicted in the corresponding plots (Fig. 6.5), provides a suitable description of this behavior.

Also the three Poisson's ratios $\nu_{\rm RT}$, $\nu_{\rm TL}$, $\nu_{\rm LR}$ are time-dependent material parameters. In contrast to the relaxation and viscoelastic shear moduli, the real parts of the two Poisson's ratios $\nu_{\rm RT}$ and $\nu_{\rm LR}$ increase in the LC domain with decreasing frequency, while their complex parts have negative signs. In the simplest way, involving the smallest number of model parameters, this is suitably represented by a power law model with an additional spring in parallel, where the creep exponent α has a negative sign, producing the slight increase of the two Poisson's ratios in the time domain with time. The Poisson's ratio in the tangential-longitudinal direction, $\nu_{\rm TL}$, increases with increasing frequency. This behavior again can be described by a power law model, this time with a positive exponent α .

After definition of a macroscopic rheological model, the associated model parameters



Figure 6.5: Cole-Cole diagrams for different viscoelastic material parameters predicted by the multiscale homogenization model and suitable macroscopic rheological models: (a) radial relaxation modulus $E_{\rm R}$, (b) tangential relaxation modulus $E_{\rm T}$, (c) longitudinal relaxation modulus $E_{\rm L}$, (d) radial-tangential shear relaxation modulus $G_{\rm RT}$, (e) tangential-longitudinal shear relaxation modulus $G_{\rm TL}$, (f) longitudinal-radial shear relaxation modulus $G_{\rm LR}$, (g) radial-tangential Poisson's ratio $\nu_{\rm RT}$, (h) tangentiallongitudinal Poisson's ratio $\nu_{\rm TL}$, (i) longitudinal-radial Poisson's ratio $\nu_{\rm LR}$. Calculated for spruce with a density of $\rho_{\rm wood}^{\rm dry} = 450 \,\rm kg/m^3$, a moisture content of $MC = 10 \,\%$, and a microfibril angle of $\bar{\theta} = 15^{\circ}$.

can be easily obtained by minimizing the error between the predictions of the chosen rheological model and the pointwise estimated creep behavior for different times. For the spruce wood example shown in Fig. 6.5, the parameters are listed in Table 6.2 for the according equations given in Fig. 6.1.

Table 6.2: Rheological models and associated model parameters fitted to multiscale predictions (see Fig. 6.1) for the nine independent viscoelastic material parameters of wood. Parameters specified for spruce with a dry density of 450 kg/m^3 , a moisture content of 10%, and a microfibril angle of 15°.

Material parameter	rheological model	$\mu_p \; [\text{GPa}]$	$\mu_0 \; [\text{GPa}]$	$J_a \; [\mathrm{GPa}^{-1}]$	α
$E_{\rm R}$	power-law	-	0.6841	$0.0365 \ (t_a = 1 \mathrm{s})$	0.2064
E_{T}	power-law	-	0.6293	$0.0398 \ (t_a = 1 \mathrm{s})$	0.2065
$E_{\rm L}$	fractional Zener	10.527	1.6387	$0.0167 \ (t_a = 1 \mathrm{s})$	0.2121
$G_{ m RT}$	power-law	-	0.0777	$0.3209 \ (t_a = 1 \mathrm{s})$	0.2067
G_{TL}	fractional Zener	0.3189	0.3511	$0.0816 \ (t_a = 1 \mathrm{s})$	0.2129
$G_{ m LR}$	fractional Zener	0.3014	0.3318	$0.0861 \ (t_a = 1 \mathrm{s})$	0.2129
Material parameter	rheological model	$\mu_p \ [1]$	μ_0 [1]	J_a [1]	α
$ u_{ m RT}$	fractional Zener	0.6231	0.0458	1358.2 ($t_a = 1 s$)	-0.2153
$ u_{\mathrm{TL}}$	power-law	-	0.0141	$0.5770 \ (t_a = 1 \mathrm{s})$	0.2268
$ u_{ m LR}$	fractional Zener	0.2572	0.1214	275.95 $(t_a = 1 s)$	-0.2155

6.8 Summary

In this chapter, a multiscale model for the prediction of viscoelastic material properties of softwood is presented. The starting point is the viscoelastic behavior of the ligninhemicellulose matrix under shear load on the molecular scale, which is described by a so-called power-law model. Through revisiting the morphology of softwood across different length scales, the viscoelastic properties of polymer network, cell wall, and softwood are determined. The orthotropic material behavior of softwood with nine independent material functions is successfully derived from the (isotropic) viscoelastic shear behavior of the lignin-hemicellulose phase. The viscoelastic model parameters obtained for softwood by the multiscale model are compared with respective experimental data, showing a considerably good prediction quality for both initial compliance and time-dependent increase of compliance of the model, especially for shear loading and loading in radial and tangential material directions. For each material parameter (relaxation moduli, shear moduli, Poisson's ratios), the model yields a characteristic viscoelastic behavior that can be described by macroscopic rheological models. The presented model thus allows for prediction of sets of viscoelastic material parameters for a specific sample of softwood suitable for further macroscopic calculations.

Chapter 7

Sorption

In this chapter, a mathematical description of sorption is given. After a short recapitulation of the background of this process, a sub-model on the cell wall scale is derived. This model allows for description of the time-dependence of sorption based on a diffusion process across the cell wall. To quantify sorption hysteresis, a suitable empirical model that is also used in the numerical approach presented in Chapter 9 is given. In addition, a possible theoretical description for sorption hysteresis based on physical assumptions is given.

7.1 Introduction

Sorption is the phase change process between water vapor and bound water. It is driven by differences in chemical potentials, which are functions of mechanical pressure, concentration, and temperature. When the concentrations of bound water and water vapor are constant in time, equilibrium is reached. In wood, this equilibrium is not unique, but dependent on moisture content history, resulting in a pronounced sorption hysteresis effect.

Sorption in wood is different from the capillary force driven sorption in other porous materials, since the driving force for sorption is primarily of chemical nature [27]. The wood polymers, making up the solid part of the cell wall, are interconnected mainly by hydrogen bonds between hydroxyl groups. The unbounded hydroxyl groups have a great affinity to water and are thus the reason for sorption in wood. Each of this hydroxyl groups constitutes a possible place for adsorbed water molecules, accordingly they are also called sorption sites. Adsorption of bound water is accompanied by swelling of the cell walls and – partially – breaking of hydrogen bonds between the wood polymers. Upon this breaking additional sorption sites become accessible and even more water may get adsorbed [27]. Upon desorption, the broken hydrogen bonds will re-establish, but since bound water molecules occupy parts of the involved sorption sites, this process will be delayed [27]. This is the commonly accepted reason for sorption hysteresis: during

desorption wood is able to contain more bound water at a preset relative humidity than during adsorption.

In the author's opinion the time dependence of sorption has two reasons. On the one hand the transport process inside the cell wall takes time, while on the other hand the time-dependent mechanical behavior of the cell wall also affects the time that is needed to reach the final equilibrium state. The second may be observed in the investigation of very small specimen (see e.g. [42]), a possible theoretical explanation for this effect is given in Section 7.4. As for the transport process inside the cell wall, an according sub-model is derived in the following section.

7.2 Microscale sub-model for the cell wall

The sorption rate \dot{c} , that mathematically describes the exchange of water between the two water phases (bound water in the cell wall and water vapor in the lumens), cannot be suitably captured on the macroscale because of its microscale origin. However, a correct description is possible on a length scale where the two water phases can be distinguished spatially. Thus, a single tracheid cell is examined. The microscopic distribution of bound water inside the cell wall, $\hat{c}_b(\mathbf{x}, t)$, follows from Fick's second law of diffusion, reading as

$$\frac{\partial \hat{c}_b}{\partial t} = \frac{\partial}{\partial \mathbf{x}} \cdot \left[\mathbf{D}_{\text{cwm}}(\hat{c}_b) \frac{\partial \hat{c}_b}{\partial \mathbf{x}} \right] + \dot{m}_b, \tag{7.1}$$

where \dot{m}_b denotes an internal volumetric source term due to the macroscopic flux and $\mathbf{D}_{\rm cwm}$ the diffusion tensor of bound water in the cell wall material. Main gradients inside the cell wall due to sorption develop mainly in through-thickness direction of the cell wall. Therefore the transport problem through a cell wall arising from sorption can be approximately treated as axisymmetric, considering the cross-section of the cell as circular ring as shown in Figure 7.1(b). Therein, the outer radius r_2 is taken as the average radius of the tracheid, lying in the range of 10 to 25 µm. The inner radius r_1 follows from

$$r_2^2 \pi f_{\text{lum}} = r_1^2 \pi \quad \Rightarrow \quad r_1 = r_2 \sqrt{f_{\text{lum}}},\tag{7.2}$$

where f_{lum} again denotes the volume fraction of the lumens.

Moreover, the tracheids show a by far larger longitudinal dimension compared to their cross-sectional dimensions. Microscale variations of the transport process along the cell can be neglected for this reason, and the tracheids are treated as circular cylinders. Therefore the originally three-dimensional problem [Eq. (7.1)] simplifies to a one-dimensional one when formulated in a cylindrical coordinate system, since \hat{c}_b depends under these assumptions only on the radial coordinate r:

$$\frac{\partial \hat{c}_b}{\partial t} = \frac{\partial}{\partial r} \left(D_{\text{cwm,r}} \frac{\partial \hat{c}_b}{\partial r} \right) + \dot{m}_b, \tag{7.3}$$

 $D_{\text{cwm,r}}$ denotes the diffusion coefficient of bound water in pure cell wall material in the radial direction of the cell. Microscopic gradients of water vapor concentration and temperature are not taken into account, because they are negligibly small.



Figure 7.1: Model representation of a wood cell: (a) natural shape of wood cell, (b) simplified representation as circular cylinder

The diffusion tensor of bound water in the cell wall material, \mathbf{D}_{cwm} , is assumed to be transversely isotropic with the plane of isotropy perpendicular to the cell axis. Therefore the radial diffusion coefficient $D_{cwm,r}$ equals the transversal diffusion coefficient $D_{cwm,trans}$ (for values see [100, 95]). In principal, the diffusion properties of the cell wall are functions of bound water concentration \hat{c}_b . However, since the variation of this concentration throughout the cell wall is only very small, $D_{cwm,r}$ is assumed to be constant with respect to r in Eq. (7.3).

At the interface of cell walls and lumens, the microscopic concentration of bound water in the cell wall, \hat{c}_b , is in local equilibrium with the water vapor concentration inside the lumen according to a sorption isotherm. This yields the first boundary condition for the



Figure 7.2: Microscopic distribution of bound water concentration in radial direction problem at the inner side of the cell wall, reading as

$$\left. \hat{c}_b \right|_{r=r_1} = \rho_{\rm cwm}^{\rm dry} EMC(c_v, T), \tag{7.4}$$

where $\rho_{\rm cwm}^{\rm dry}$ denotes the dry density of the cell wall with approximately 1500 kg/m³ [95] and $EMC(c_v, T)$ the equilibrium moisture content (see Fig. 7.2). As indicated, EMC is a

function of water vapor concentration c_v and temperature T. It may be calculated based on a sorption isotherm, to describe sorption hysteresis the empirical approach given in the following section may be used. Accounting only for microscopic fluxes towards the cell wall surface, in the middle of the cell wall a Neumann boundary condition is applied:

$$\left. \frac{\partial \hat{c}_b}{\partial r} \right|_{r=r_2} = 0. \tag{7.5}$$

The microscopic flow across the cell wall quickly approaches steady-state conditions. Therefore the time derivative of \hat{c}_b in Eq. (7.3) can be set to zero, resulting in

$$\frac{\partial}{\partial r} \left(D_{\text{cwm,r}} \frac{\partial \hat{c}_b}{\partial r} \right) + \dot{m}_b = 0.$$
(7.6)

Integration of Eq. 7.6 with respect to r yields

$$D_{\text{cwm,r}} \frac{\partial \hat{c}_b}{\partial r} + \int \dot{m}_b \, \mathrm{d}r = D_{\text{cwm,r}} \frac{\partial \hat{c}_b}{\partial r} + \dot{m}_b \, r + C_1 = 0.$$
(7.7)

Evaluating Eq. (7.7) for $r = r_2$ and considering the boundary condition specified in Eq. (7.5), the constant of integration, C_1 , follows as

$$\dot{m}_b r_2 + C_1 = 0, \qquad C_1 = -\dot{m}_b r_2.$$
 (7.8)

Inserting Eq. (7.8) into Eq. (7.7) thus yields

$$D_{\rm cwm,r} \frac{\partial \hat{c}_b}{\partial r} + \dot{m}_b r - \dot{m}_b r_2 = 0.$$
(7.9)

Dividing Eq. (7.9) by D_{cwm} and integrating again with respect to r gives the microscopic distribution of bound water as

$$\hat{c}_b = \int \left(-\frac{\dot{m}_b}{D_{\rm cwm,r}} r + \frac{\dot{m}_b r_2}{D_{\rm cwm}} \right) \, \mathrm{d}r = -\frac{\dot{m}_b}{2 \, D_{\rm cwm,r}} \, r^2 + \frac{\dot{m}_b r_2}{D_{\rm cwm,r}} \, r + C_2. \tag{7.10}$$

The second constant of integration C_2 is derived from the boundary condition stated in Eq. (7.4) as

$$C_2 = \rho_{\rm cwm}^{\rm dry} EMC + \frac{\dot{m}_b r_1^2}{2 D_{\rm cwm}} - \frac{\dot{m}_b r_1 r_2}{D_{\rm cwm,r}}.$$
(7.11)

Inserting Eq. (7.11) into Eq. (7.10) yields the solution of the differential equation (7.6)

$$\hat{c}_b(r) = -\frac{\dot{m}_b}{2 D_{\text{cwm,r}}} r^2 + \frac{\dot{m}_b r_2}{D_{\text{cwm,r}}} r + \rho_{\text{cwm}}^{\text{dry}} EMC + \frac{\dot{m}_b r_1^2}{2 D_{\text{cwm,r}}} - \frac{\dot{m}_b r_1 r_2}{D_{\text{cwm,r}}} = \frac{\dot{m}_b}{2 D_{\text{cwm,r}}} \left(-r^2 + 2 r_2 r + r_1^2 - 2 r_1 r_2 \right) + \rho_{\text{cwm}}^{\text{dry}} EMC.$$
(7.12)

0

The link between the microscopic and the macroscopic moisture transport problem is established by claiming equality of the integrals of the microscopic bound water concentration $\hat{c}_b(r)$ and of the macroscopic bound water concentration c_b over the volume V of a tracheid (calculated for unit length):

$$\int_{V} \hat{c}_{b} \, \mathrm{d}V = \int_{V} c_{b} \, \mathrm{d}V,$$

$$\int_{r_{1}}^{r_{2}} \int_{0}^{2\pi} r \, \hat{c}_{b} \, \mathrm{d}\varphi \, \mathrm{d}r = c_{b} \, \pi \left(r_{2}^{2} - r_{1}^{2}\right).$$
(7.13)

The only remaining unknown variable in Eq. (7.12) is the internal volumetric source term \dot{m}_b . Using Eq. (7.12) in Eq. (7.13) yields

$$c_{b} = \frac{1}{\pi \left(r_{2}^{2} - r_{1}^{2}\right)} \int_{r_{1}}^{r_{2}} \int_{0}^{2\pi} r \, \hat{c}_{b} \, \mathrm{d}\varphi \, \mathrm{d}r$$

$$= \frac{2}{\left(r_{2}^{2} - r_{1}^{2}\right)} \int_{r_{1}}^{r_{2}} \left[\frac{\dot{m}_{b}}{2 \, D_{\mathrm{cwm,r}}} \left(-r^{2} + 2 \, r_{2} \, r + r_{1}^{2} - 2 \, r_{1} \, r_{2}\right) + \rho_{\mathrm{cwm}}^{\mathrm{dry}} \, EMC\right] r \, \mathrm{d}r$$

$$= \frac{\dot{m}_{b} \left(5 \, r_{2}^{3} - 7 \, r_{1} \, r_{2}^{2} - r_{1}^{2} \, r_{2} + 3 \, r_{1}^{3}\right)}{12 \, D_{\mathrm{cwm,r}} \left(r_{2} + r_{1}\right)} + \rho_{\mathrm{cwm}}^{\mathrm{dry}} \, EMC.$$
(7.14)

Rearranging Eq. (7.14) allows to eliminate the unknown internal volumetric source term \dot{m}_b by

$$\dot{m}_b = \frac{12 D_{\text{cwm,r}} \left(r_2 + r_1 \right) \left(c_b - \rho_{\text{cwm}}^{\text{dry}} EMC \right)}{5 r_2^3 - 7 r_1 r_2^2 - r_1^2 r_2 + 3 r_1^3}.$$
(7.15)

Inserting Eq. (7.15) in Eq. (7.12) yields the final equation for the microscopic distribution of bound water in the cell wall as

$$\hat{c}_b(r) = \frac{6\left(r_2 + r_1\right)\left(c_b - \rho_{\rm cwm}^{\rm dry} EMC\right)}{5\,r_2^3 - 7\,r_1\,r_2^2 - r_1^2\,r_2 + 3\,r_1^3} \left(-r^2 + 2\,r_2\,r + r_1^2 - 2\,r_1\,r_2\right) + \rho_{\rm cwm}^{\rm dry} EMC.$$
(7.16)

Finally, the sought sorption rate \dot{c} is derived as the flux across the inner interface between lumen and cell wall. This flux can be calculated by evaluating Fick's first law of diffusion at the cell wall surface:

$$\dot{c} = -\frac{A_i}{V_{cwm}} D_{cwm,r} f_{cwm} \left. \frac{\partial \hat{c}_b}{\partial r} \right|_{r=r_1} = -\frac{2 r_1}{r_2^2 - r_1^2} D_{cwm,r} f_{cwm} \left. \frac{\partial \hat{c}_b}{\partial r} \right|_{r=r_1}.$$
(7.17)

In Eq. (7.17), the volume fraction $f_{\rm cwm}$ relates the sorption rate to the total volume of wood instead of volume of pure cell wall material. This is due to the definition of \dot{c} , see Section 3.1.1. Inserting Eq. (7.15) in Eq. (7.12) and subsequently in Eq. (7.17), the coupling term \dot{c} finally follows under consideration of Eq. (7.2) as

$$\dot{c} = -\frac{2r_1}{r_2^2 - r_1^2} D_{\text{cwm,r}} f_{\text{cwm}} \frac{6(r_2 + r_1) \left(c_b - \rho_{\text{cwm}}^{\text{dry}} EMC\right)}{5r_2^3 - 7r_1r_2^2 - r_1^2r_2 + 3r_1^3} \left(-2r_1 + 2r_2\right) = \frac{24 D_{\text{cwm,r}} f_{\text{cwm}} \left(\rho_{\text{cwm}}^{\text{dry}} EMC - c_b\right) f_{\text{lum}}^{\frac{1}{2}}}{r_2^2 \left(5 - 7f_{\text{lum}}^{\frac{1}{2}} - f_{\text{lum}} + 3f_{\text{lum}}^{\frac{3}{2}}\right)}.$$
(7.18)

In order to check this approach, macroscopic steady state conditions are considered, where \dot{c} must equal zero. Such conditions imply that $c_b = \rho_{\rm cwm}^{\rm dry} EMC$ across the cell wall, making \dot{c} in Eq. (7.18) to vanish. This confirms the plausibility of Eq. (7.18).

7.3 Empirical description of sorption hysteresis

Due to the pronounced hysteresis observed in sorption processes, several empirical models were developed in the last decades [28] to describe this phenomenon. In this section, the approach developed by Frandsen et al. [27, 28] is reproduced. It provides a good description of the hysteresis phenomena observed for the equilibrium moisture content. In addition it doesn't require a history variable and has advantages regarding numerical stability and time integration in numerical models, see Subsection 9.4.3 in Chapter 9.



Figure 7.3: Graphical representation of Frandsen's hysteresis model: equilibrium moisture content $EMC(\varphi)$ (i.e. the sorption isotherm) and parameter $s(\varphi)$ for (a) adsorption and (b) desorption. The curves $MC_a(\varphi)$ and $MC_d(\varphi)$ are the boundary curves for adsorption and desorption, respectively.

The main idea is that the equilibrium moisture content $EMC(\varphi)$ can be described in closed form as

$$EMC(\varphi) = MC_a(\varphi) + \left[MC_d(\varphi) - MC_a(\varphi)\right]s(\varphi),$$
(7.19)

where $MC_a(\varphi)$ and $MC_d(\varphi)$ are the adsorption and desorption boundary curves, respectively, and $\varphi = c_v/c_{v,sat}(T)$ denotes the relative humidity. The dimensionless parameter $s(\varphi)$ can take values between 0 and 1. Reformulating Eq. (7.19), s can be calculated as

$$s(\varphi) = \frac{EMC(\varphi) - MC_a(\varphi)}{MC_d(\varphi) - MC_a(\varphi)}.$$
(7.20)

Apparently, for s = 0 the equilibrium moisture content equals the adsorption scanning curve, i.e. $EMC(\varphi) = MC_a(\varphi)$, while for s = 1 it equals the desorption scanning curve, i.e. $EMC(\varphi) = MC_d(\varphi)$. Starting from an initial state given by φ_0 and s_0 , the actual

parameter s follows from

$$s(\varphi) = \begin{cases} -1 + 2^{\left(\frac{1-\varphi}{1-\varphi_d^0}\right)^{\left(\frac{d_1}{\ln[d_2(1-\varphi_d^0)]}\right)}} & (\dot{\varphi} > 0) \land (s_0 > 0) & \text{induces for a strength}} \\ 0 & (\dot{\varphi} > 0) \land (s_0 = 0) & \text{or a strength for a strength$$

with

$$\varphi_a^0 = \varphi_0 \left(d_2 \, \varphi_0 \right)^{q_1},\tag{7.22}$$

$$\varphi_d^0 = 1 - (1 - \varphi_0) \left[d_2 \left(1 - \varphi_0 \right) \right]^{q_2}, \tag{7.23}$$

and

$$q_1 = -\frac{\ln\left[\ln(2)\right] - \ln\left[\ln(2 - s_0)\right]}{\ln\left[\ln(2)\right] - \ln\left[\ln(2 - s_0)\right] - d_1},\tag{7.24}$$

$$q_2 = -\frac{\ln\left[\ln(2)\right] - \ln\left[\ln(1+s_0)\right]}{\ln\left[\ln(2)\right] - \ln\left[\ln(1+s_0)\right] - d_1}.$$
(7.25)

In Eqs. (7.21) to (7.25), d_1 and d_2 are parameters defining the shape of the scanning curves. In addition, the adsorption and desorption boundary curves have to be defined. In this context, the Hailwood-Horrobin isotherm proved to be suitable, which is defined as

$$MC_{\alpha}(\varphi) = \frac{\varphi}{f_1^{\alpha} + f_2^{\alpha} \varphi + f_3^{\alpha} \varphi^2}, \quad \alpha \in \{a, d\}.$$
(7.26)

The shape parameters f_i^{α} have to be calibrated to experimental results.

7.4 Theoretical description of sorption hysteresis

Although the empirical description of sorption hysteresis presented in the previous section is capable to suitably reproduce macroscopic experimental findings, its general applicability is not assured due to its lack of physical background. In this section, a theory is proposed that provides a possible description of sorption hysteresis. It incorporates the time-dependent mechanical work due to shrinkage and swelling of the cell wall by accounting for the pressure dependency of the chemical potential of bound water.

7.4.1 Chemical potentials of water vapor and bound water

Starting point of the following considerations are the equal chemical potentials of water vapor and bound water at equilibrium conditions. Both potentials can be written as functions of temperature, pressure, and concentration of the according phase. For water vapor this reads as [2]

$$\mu_v = \mu_v^{\bullet} + \alpha_v \left(T - T^{\bullet} \right) + RT \ln \left(\frac{p_{\text{sat}}}{p^{\bullet}} \right) + RT \ln(\varphi), \tag{7.27}$$

where the chemical potential μ_v^{\bullet} of water vapor and the temperature coefficient α_v at standard conditions ($T^{\bullet} = 298 \text{ K}, p^{\bullet} = 101, 325 \text{ kPa}$) are specified as

$$\mu_v^{\circ} = -228.59 \,\frac{\text{kJ}}{\text{mol}}, \quad \alpha_v = -188.72 \,\frac{\text{J}}{\text{mol K}}.$$
(7.28)

In Eq. (7.27), T denotes the temperature in [K], R is the universal gas constant, and p_{sat} the saturation vapor pressure at given temperature. Accordingly, the second term in Eq. (7.27) accounts for changes in chemical potential upon temperature changes, the third term for changes upon pressure changes, while the fourth term describes the concentration-dependency of the chemical potential of water vapor. Fig. 7.4(a) exemplarily shows this concentration-dependency for water vapor at a temperature of 23 °C and a pressure of 101.325 kPa.

Also the chemical potential of bound water is a function of temperature T, concentration, now expressed in terms of moisture content MC, and pressure p_b . In contrast to water vapor exact values are not available. However, based on a chemical potential $\mu_{b,0}$ at known initial conditions $(T_0, MC_0, p_{b,0})$, the chemical potential μ_b can be linearized as

$$\mu_b = \mu_{b,0} + \alpha_b \left(T - T_0 \right) + \beta_b \left(p_b - p_{b,0} \right) + \gamma_b \left(MC - MC_0 \right).$$
(7.29)

From a Maxwell relation it follows that the pressure coefficient β_b equals molar volume of bound water. In addition the concentration coefficient γ_b is the derivative of the nonlinearized equation for chemical potential ($\mu_b = \mu_{b,0} + RT \ln \frac{MC}{MC_0} + \dots$) with respect to moisture content MC at point MC_0 . Thus the coefficients β_b and γ_b can be calculated as

$$\beta_b = \frac{M_{\rm H_2O}}{\rho_b}, \qquad \gamma_b = \frac{RT}{MC_0}, \tag{7.30}$$

with $M_{\rm H_2O} = 18.02 \,\text{g/mol}$ denoting the molar mass of water, while ρ_b is the density of bound water [44]. Based on these coefficients, Fig. 7.4(b) shows several isobars at a temperature of of 23 °C.

In the following, a very small sample of wood (negligible influence of time-dependent transport processes inside the sample) and ideal Dirichlet boundary conditions (direct specification of relative humidity φ and temperature T at the surface of the sample) are assumed. Under equilibrium conditions, $\mu_v = \mu_b$ must apply. Therefore, when the chemical potential of water vapor changes upon a shift in relative humidity, also the chemical potential of bound water will change. Assuming isothermal conditions $T = T_0$ (that are motivated based on the much faster temperature equilibration than the time-dependent deformations), solely the pressure p_b and the moisture content MCwill change. Initially, conditions will arise according to the elastic compliance of the cell wall. This is depicted in Fig. 7.4 for a drop in chemical potential as "initial change": Some water is removed from the cell wall, leading to a lower moisture content, but also to a negative strain inside the cell wall, which further causes a negative pressure change



Figure 7.4: Chemical potentials of (a) water vapor and (b) bound water as functions of concentrations φ and MC and pressure change $(p_b - p_{b,0})$ in case of bound water. The curve of chemical potential μ_b for zero pressure is backcalculated based on a typical sorption isotherm of wood. The solid red lines denote an initial change in chemical potential upon a drop in relative humidity, while the dashed red line depicts the timedependent change in moisture content due to the time-dependent compliance of the cell wall.

in the bound water phase. Certainly – as shown in Chapter 6 – the compliance of the cell wall is not only elastic. Therefore stress relaxation will occur: the absolute value of pressure will be reduced with time, accompanied by a further decrease in moisture content. During this process, the chemical potential of bound water is always constant because of the equilibrium with the water vapor phase. By contrast the moisture content is not constant but a function of time – the derivation of this function is the aim of this section.

So far, pressure p_b and moisture content MC constitute two independent variables. In the following subsection, they will be linked using poromechanical considerations.

7.4.2 Moisture content as function of pore pressure

Poromechanics allows to describe the macroscopic stress Σ of a material as function of macroscopic strain **E** and bound water pressure p_b . In general terms, poromechanics under saturated conditions – i.e. all "pores" completely filled with "liquid" – captures changes of amounts of this liquid via eigenstrains in an RVE (for wood starting in the polymer network). In an existing poromechanical model for wood [4], the actual liquid state is expressed in terms of pore pressure p_b . Admittedly, the concept of "pores" and according "pore pressure" in the wood cell wall is worth discussing, whereas eigenstrains due to changes in moisture content are reasonable. In this subsection poromechanics is just used as a tool to explain the influence of the mechanical behavior of the cell wall on the equilibrium moisture state through according eigenstrains, which is also possible with the existing poromechanical formulation. Excluding plastic strains, the according equation [resulting from Eq. (3.18)] reads as

$$\boldsymbol{\Sigma} = \mathbb{C} : \mathbf{E} - \mathbf{b}(p_b - p_{b,0}). \tag{7.31}$$

Specifying this equation for free shrinkage and swelling (i.e. $\Sigma = 0$) allows to express the strain tensor as function of the change in pore pressure,

$$\mathbf{E} = \mathbb{C}^{-1} : \mathbf{b}(p_b - p_{b,0}). \tag{7.32}$$

Using this relation in the second state equation of poromechanics [4] gives the change in cell wall porosity $(\phi - \phi_0)$ as function of pressure change $(p_b - p_{b,0})$ as

$$\phi - \phi_0 = \mathbf{b} : \mathbf{E} + \frac{1}{N} (p_b - p_{b,0})$$

= $\mathbf{b} : \mathbb{C}^{-1} : \mathbf{b} (p_b - p_{b,0}) + \frac{1}{N} (p_b - p_{b,0})$
= $J(p_b - p_{b,0}),$ (7.33)

with N denoting the Biot modulus. For convenience, the variable J is introduced, which can be interpreted as "sorption compliance" of the cell wall:

$$J = \mathbf{b} : \mathbb{C}^{-1} : \mathbf{b} + \frac{1}{N}.$$
(7.34)

Like \mathbb{C} and **b**, also J is a function of moisture content. J – as defined in Eq. (7.34) – is a purely elastic quantity depending on the definition of \mathbb{C} and **b**. However, only the initial mechanical behavior of wood is elastic (see Chapter 6), followed by an additional time-dependent compliance. Therefore it is obvious to assume that J exhibits a timedependent behavior as well. Presuming a power-law type behavior as it is suitable for other mechanical parameters (see Chapter 6), the time-dependent sorption compliance J(t) can be expressed as

$$J(t) = J_0 + J_a \left(\frac{t}{t_a}\right)^{\alpha}.$$
(7.35)

For small changes in pressure (neglecting the dependence of J on pressure), the timedependent change of pore space can be given as

$$\phi(t) = \phi_0 + \int_0^t J(t-\tau) \,\dot{p}_b(\tau) \,\mathrm{d}\tau.$$
(7.36)

In the following, "saturated conditions" in poromechanical terms are assumed. This implies that the pore space is completely filled with "fluid". Accordingly, the moisture content MC is directly related to porosity ϕ . In good approximation, this relation is linear (see Fig. 5 in [4]); in combination with Eq. (7.36), this allows to express moisture content as time-dependent function of bound water pressure:

$$MC(t) = MC_0 + \frac{\partial MC}{\partial \phi} \int_0^t J(t-\tau) \dot{p}_b(\tau) \,\mathrm{d}\tau, \qquad (7.37)$$

where the initial moisture content MC_0 equals $(\partial MC/\partial \phi)\phi_0$. This equation constitutes the missing link between moisture content and bound water pressure. In the next subsection, an analytical solution for the evolution of moisture content due to steps in relative humidity is derived therefrom.

7.4.3 Time-dependent evolution of moisture content due to steps in relative humdity

When determining a sorption isotherm, relative humidity usually is changed stepwise. This results in according steps in chemical potential of water vapor. For one step $\Delta \mu$ at time t = 0, the function of chemical potential can be written as

$$\mu_v(t) = \mu_{v,0} + \Delta \mu^{(0)} \Theta(t), \tag{7.38}$$

where $\mu_{v,0}$ is the initial chemical potential of water vapor and $\Theta(t)$ is the Heaviside step function, which is defined as

$$\Theta(t) = \begin{cases} 0 & \text{for } t < 0\\ 1 & \text{for } t \ge 0 \end{cases}$$

$$(7.39)$$

Obligatory, the chemical potential of bound water must be equal to that of water vapor, i.e. $\mu_v(t) = \mu_b(t)$. Under isothermal conditions and under consideration of $\mu_{b,0} = \mu_{v,0}$, combination of Eq. (7.38) with Eq. (7.29) therefore yields

$$\mu_b(t) = \mu_{b,0} + \Delta \mu^{(0)} \Theta(t) = \mu_{b,0} + \beta_b \left(p_b(t) - p_{b,0} \right) + \gamma_b \left(MC(t) - MC_0 \right).$$
(7.40)

Canceling the initial chemical potential $\mu_{b,0}$, considering an initial condition $p_{b,0} = 0$, and substituting *MC* with the expression specified in Eq. (7.37) yields a differential equation for the pressure $p_b(t)$:

$$\Delta \mu^{(0)} \Theta(t) = \beta_b \, p_b(t) + \gamma_b \frac{\partial MC}{\partial \phi} \int_0^t J(t-\tau) \, \dot{p}_b(\tau) \, \mathrm{d}\tau.$$
(7.41)

A direct solution of this differential equation is not available. Therefore it is tried to obtain the solution in the Laplace-Carson domain. Applying the Laplace-Carson transform as defined in Eq. (6.5) to Eq. (7.41) yields

$$\Delta \mu^{(0)} = \beta_b \, p_b^*(s) + \gamma_b \frac{\partial MC}{\partial \phi} J^*(s) \, p_b^*(s). \tag{7.42}$$

Inserting the LC transform (see Fig. 6.1) of the sorption compliance as defined in Eq. (7.35) into Eq. (7.42) yields

$$\Delta\mu^{(0)} = \beta_b \, p_b^*(s) + \gamma_b \frac{\partial MC}{\partial \phi} J_0 \, p_b^*(s) + \gamma_b \, J_a \left(\frac{1}{s \, t_a}\right)^{\alpha} \Gamma \left(1 + \alpha\right) \, p_b^*(s) \tag{7.43}$$

Rearrangement of this equation results in the sought expression for pressure $p_b^*(t)$ in the LC domain:

$$p_b^*(s) = \frac{\Delta \mu^{(0)}}{\beta_b + \gamma_b \frac{\partial MC}{\partial \phi} J_0 + \gamma_b \frac{\partial MC}{\partial \phi} J_a \left(\frac{1}{s t_a}\right)^{\alpha} \Gamma\left(1 + \alpha\right)}.$$
(7.44)

The according representation in the Laplace domain is derived by dividing this equation by the complex variable s:

$$\hat{p}_b(s) = \frac{\Delta \mu^{(0)} s^{-1}}{\beta_b + \gamma_b \frac{\partial MC}{\partial \phi} J_0 + \gamma_b \frac{\partial MC}{\partial \phi} J_a \left(\frac{1}{s t_a}\right)^{\alpha} \Gamma\left(1 + \alpha\right)}$$
(7.45)

For this function no tabulated back-transform exists. Therefore, Eq. (7.45) is developed in a Taylor series $(\frac{1}{1+x} = \sum_{k=0}^{\infty} (-1)^k x^k$ for |x| < 1; since a series in the Laplace domain can be inversely transformed in a term-wise manner:

$$\hat{p}_{b}(s) = \frac{\Delta\mu^{(0)}s^{-1}\left(\beta_{b} + \gamma_{b}\frac{\partial MC}{\partial\phi}J_{0}\right)^{-1}}{1 + \frac{\gamma_{b}\frac{\partial MC}{\partial\phi}J_{a}}{\beta_{b} + \gamma_{b}\frac{\partial MC}{\partial\phi}J_{0}}\left(\frac{1}{st_{a}}\right)^{\alpha}\Gamma\left(1+\alpha\right)}$$

$$= \Delta\mu^{(0)}s^{-1}\left(\beta_{b} + \gamma_{b}\frac{\partial MC}{\partial\phi}J_{0}\right)^{-1}\sum_{k=0}^{\infty}(-1)^{k}\left[\frac{\gamma_{b}\frac{\partial MC}{\partial\phi}J_{a}}{\beta_{b} + \gamma_{b}\frac{\partial MC}{\partial\phi}J_{0}}\left(\frac{1}{st_{a}}\right)^{\alpha}\Gamma\left(1+\alpha\right)\right]^{k}$$

$$= \Delta\mu^{(0)}\sum_{k=0}^{\infty}(-1)^{k}\frac{\left(\gamma_{b}\frac{\partial MC}{\partial\phi}J_{a}\right)^{k}}{\left(\beta_{b} + \gamma_{b}\frac{\partial MC}{\partial\phi}J_{0}\right)^{k+1}}\left(\frac{1}{t_{a}}\right)^{\alpha k}\left[\Gamma\left(1+\alpha\right)\right]^{k}\frac{1}{s^{\alpha k+1}}.$$
(7.46)

For this series, the term-wise transformation to the time-domain reads as:

$$p_b(t) = \Delta \mu^{(0)} \sum_{k=0}^{\infty} (-1)^k \frac{\left(\gamma_b \frac{\partial MC}{\partial \phi} J_a\right)^k}{\left(\beta_b + \gamma_b \frac{\partial MC}{\partial \phi} J_0\right)^{k+1}} \left(\frac{1}{t_a}\right)^{\alpha k} \left[\Gamma\left(1+\alpha\right)\right]^k \frac{t^{\alpha k}}{\Gamma(1+\alpha k)} \quad (7.47)$$
$$= \Delta \mu^{(0)} R(t), \quad (7.48)$$

where the abbreviation R(t) is introduced for convenience. Eq. (7.47) converges for

$$t < t_a \left[\frac{\beta_b + \gamma_b \frac{\partial MC}{\partial \phi} J_0}{\gamma_b \frac{\partial MC}{\partial \phi} J_a \Gamma(1+\alpha)} \right]^{\frac{1}{\alpha}}.$$
(7.49)

Eq. (7.47) describes the time-dependent evolution of p_b due to one step in chemical potential. It is a linearized approach and therefore only valid for small steps in chemical potential. Applying the Boltzmann superposition principle, this approach can be generalized for n steps as

$$p_b(t) = p_{b,0} R(t) + \sum_{i=0}^n \Delta \mu^{(i)} R(t - t_i) \Theta(t - t_i).$$
(7.50)

This equation allows to calculate the actual pressure $p_b(t)$ for several steps in chemical potential. Hence, the evolution of moisture content, MC(t), follows from Eq. (7.40) as

$$MC(t) = MC_0 + \frac{\sum_{i=0}^{n} \Delta \mu^{(i)} \Theta(t - t_i) - \beta_b \left(p_b(t) - p_{b,0} \right)}{\gamma_b}.$$
(7.51)

7.4.4 Numerical example

In order to validate the theoretical approach presented in the previous subsections, a numerical example is evaluated and compared to corresponding experimentally derived results. The latter are taken from an experiment that was conducted to define the sorption isotherm for a piece of wood. Fortunately, also the time instants of the measurements were logged in detail. The required parts of the experimental results are summarized in Table 7.1.

Table 7.1: Experimental results derived during determination of a sorption isotherm: absolute time t_i , relative humidity $\varphi^{(i)}$, step in relative humidity $\Delta \varphi^{(i)}$, and measured moisture content $MC_{\exp}^{(i)}$ at each time instance. In either case the steps in relative humidity were applied after measuring the moisture content. The sample was a piece of spruce wood with a dry density of 400 kg/m^3 . Temperature during the experiment was 23 °C.

time instance		$13.12.2010 \\ 08:55$	$15.12.2010 \\ 09:25$	17.01.2011 18:00	20.12.2010 09:15	22.12.2010 15:00	03.01.2011 11:25	05.01.2011 15:40	07.01.2011 18:20	10.01.2011 09.15	$\frac{11.01.2011}{17:55}$
i		-3	-2	-1	0	1	2	3	4	5	6
t_i	[min]	-10110	-7200	-3805	0	3225	20290	23425	26465	30240	32200
$\varphi^{(i)}$	[%]	95	85	75	65	50	35	50	65	50	35
$\Delta \varphi^{(i)}$	[%]	-10	-10	-10	-15	-15	+15	+15	-15	-15	
$MC_{\exp}^{(i)}$	[%]				14.3	11.5	8.8	10.4	12.9	11.1	9.1

Since the approach derived in the previous subsection is linearized, not the whole experiment is considered but only a part where relative humidity was changed from 65 % to 35 % to 65 % and to 35 % back again (instances 0 to 6), in each case with an additional measurement at 50 %. Naturally, also the preceding humidity steps influence the results, therefore also the three previous steps (denoted as time instances -3, -2, and -1) were accounted for in the calculation of pressure. The starting point t_3 was chosen since the humidity of $\varphi = 95$ % was hold for a longer time before, so preceding humidity steps should not have a significant influence on the considered period. The experimental values show a distinct hysteresis, i.e. for a relative humidity of 65 % two different moisture contents were measured ($MC_{exp}^{(0)} = 14.3$ % and $MC_{exp}^{(4)} = 12.9$ %).

For a moisture content of MC = 14.3 % and a temperature of T = 296.15 K the parameters β_b and γ_b follow from Eqs. (7.30) as

$$\beta_b = 0.0000154 \,\frac{\mathrm{m}^3}{\mathrm{mol}}, \quad \gamma_b = 17200 \,\frac{\mathrm{J}}{\mathrm{mol}}.$$
 (7.52)

As for the rheological model parameters, the initial compliance J_0 was determined based on the poromechanical model given in [4] (evaluated for a dry sample density of 400 kg/m³ and a moisture content of 14.3 %) and Eq. (7.34) as $J_0 = 0.05 \,\mathrm{GPa^{-1}}$. The creep exponent was chosen in accordance with the findings in Chapter 6 as $\alpha = 0.22$. The creep compliance J_a is not directly accessible at the moment. It was suitably taken as $J_a = 0.012 \,\mathrm{GPa^{-1}}$. This choice best reproduces the experimental results, however, it is of the same order of magnitude as the values given Table 6.2 and therefore appears reasonable.

In Fig. 7.5, the results of the numerical example are displayed. Based on the chronological sequence of relative humidity, $\varphi(t)$, the chemical potential $\mu_v(t) = \mu_b(t) = \mu(t)$ is calculated based on Eq. (7.27). Accordingly, the bound water pressure $p_b(t)$ follows from Eq. (7.50), it is calculated including the relative humidity steps *i* from -3 to 5. The initial pressure $p_{b,0}$ was taken as zero, the initial moisture content was set to $MC_0 = 17.1 \%$, so that $MC(t = t_0) = 14.3 \%$. Finally, the evolution of moisture content was calculated based on Eq. (7.51).



Figure 7.5: Experimental (blue) and numerical (red) values for different parameters during a sorption experiment: relative humidity $\varphi(t)$, chemical potential of water vapor and bound water $\mu(t) = \mu_v(t) = \mu_b(t)$, bound water pressure $p_b(t)$, and moisture content MC(t).

As can be seen, the experimentally observed hysteresis (blue markers) in moisture content is suitably reproduced by the theoretical approach (red lines) – $MC(t_4)$ is lower than $MC(t_0)$ despite equal prevailing relative humidities. Further, the graph of MC(t)obviously shows that the moisture content has never reached constancy (according to the calculated lines) when it was measured during the experiment. However, at these instances the change of moisture content with time, $\partial MC/\partial t$, is between 0.02 and 0.15 % per day. This is below usual measurement precisions, so that from an "experimentalist's point of view", constant moisture content was reached. Certainly, although the moisture content is not constant, the system is in (local) equilibrium. Theoretically, the final equilibrium appears after infinite time. Since such equilibrium conditions will never be reached – not during a sorption experiment nor in life time of a structure this might be an explanation for the phenomenon of sorption hysteresis.

The usual explanation for sorption hysteresis is that the number of sorption sites is not constant but changes during adsorption and desorption. In this subsection, sorption hysteresis could be explained without consideration of this effect. Admittedly, one unknown parameter of the model (the time-dependent sorption compliance J_a) was suitably chosen to reach this model performance. Therefore it is not assured that the time-dependent deformation of the cell wall material are the only reason for sorption hysteresis. At least it could be shown that the time-dependent deformation of the cell wall has a significant influence on the sorption behavior of wood. This is also in accordance with experimental findings, e.g. Hill [42] showed that the sorption behavior of small samples shows the same mathematical structure as a creep law. The presented approach is the required theoretical background for further investigations, including intensive discussion and more comprehensive validation, e.g. by Dynamic Vapor Sorption (DVS), that allows to track the evolution of moisture content upon changes in relative humidity for very small samples, for which the time-dependent influence of transport processes on the overall observed sorption behavior is small.

Chapter 8

Additional material properties

In the previous chapters, the material properties of wood governing thermal conductivity, moisture diffusivity, viscoelasticity, and sorption were clarified. However, in the macroscopic set of equations specified in Chapter 3 several additional material properties appear. In this chapter, these missing properties needed for the description of transient transport processes (as specified in Subsection 3.5.5) are derived, in particular thermodynamic properties of solid wood, bound water, and water vapor as well as diffusion properties separated for the bound water phase and the water vapor phase.

8.1 Thermodynamic quantities

8.1.1 Specific heat capacity of wood

The specific heat capacity at constant volume c_V describes the change of internal energy e upon a change in thermodynamic temperature T. Based on statistical mechanics it was derived for dry wood by Yang [112] as

$$c_{V,\text{wood}}^{\text{dry}} = -0.60453 + 0.006714 T \quad \left[\frac{\text{kJ}}{\text{kg K}}\right].$$
 (8.1)

For wet wood, Yang gives the specific heat capacity as

$$c_{V,\text{wood}}^{\text{wet}} = \frac{c_{V,\text{wood}}^{\text{dry}} + MC \, c_{V,b}}{1 + MC},$$
(8.2)

where $c_{V,b}$ is the specific heat capacity of bound water. It was taken equal to that of liquid water, i.e. $c_{V,b} \approx 4.185 \,\mathrm{kJ \, kg^{-1} \, K^{-1}}$ [90].

8.1.2 Specific enthalpies of water vapor and bound water

The specific enthalpy of water vapor, h_v , was taken from steam tables [33]. For convenience, a polynomial was fitted to temperatures between 0 and 100 °C, reading as

$$h_v = 2060.5 + 1.3798 T + 8,4808 \times 10^{-4} T^2 \quad \left[\frac{\text{kJ}}{\text{kg}}\right].$$
 (8.3)

As for bound water, comprehensive information about enthalpies can be found in Skaar [98]. The enthalpy for bound water depends on chemical composition of the cell wall and therefore is slightly different for different wood species. For spruce [98] it is given as (converted to SI units)

$$h_b = -1143.1 + 4.185 T - 1146.4 \exp\left(-14.48 MC\right) \left[\frac{\text{kJ}}{\text{kg}}\right].$$
 (8.4)

8.2 Transport properties

In Chapters 2 and 3 it was shown that for transient processes the two water phases have to be treated separately. Therefore diffusion properties for the individual phases have to be specified. The model developed in Chapter 5 for moisture diffusivity is restricted to steady state conditions, since such conditions imply the equilibrium of the two phases. This multiscale model can be adapted for the determination of the bound water diffusion tensor \mathbf{D}_b . For this purpose the diffusion of water vapor in the lumens is deactivated in the model. This is done by setting the diffusivity of water vapor in air equal to zero. The values of the resulting macroscopic diffusion tensor thus exclusively describe bound water diffusion as observed at the macroscopic scale, incorporating tortuosity effects due to the cell structure of wood.

For use in the finite element model described in Chapter 9, estimates of the multiscale model for different bound water contents, temperatures, and densities were fitted by polynomials for each material direction, reading as

$$D_{b,i} = D_{b,i}^{\text{ref}} \left(a_{10,i} + a_{11,i} \,\overline{\rho} + a_{12,i} \,\overline{\rho}^2 + a_{13,i} \,\frac{1}{\overline{\rho}^3} \right) \cdot \left(a_{20,i} + a_{21,i} \,\overline{T} + a_{22,i} \,\overline{T}^2 + a_{23,i} \,\overline{T}^3 + a_{24,i} \,\overline{T}^4 \right) \cdot \left(a_{30,i} + a_{31,i} \,\overline{c}_b + a_{32,i} \,\overline{c}_b^2 + a_{33,i} \,\overline{c}_b^3 + a_{34,i} \,\overline{c}_b^4 \right) \\ i \in [\text{R}, \text{T}, \text{L}],$$
(8.5)

where $\overline{\rho}$, \overline{T} , and \overline{c}_b are density, temperature, and bound water concentration related to reference conditions:

$$\overline{\rho} = \frac{\rho_{\text{wood}}^{\text{dry}}}{450 \,\text{kg/m}^3}, \quad \overline{T} = \frac{T}{293.15 \,\text{K}}, \quad \overline{c}_b = \frac{c_b}{200 \,\text{kg/m}^3}. \tag{8.6}$$

 $D_{b,i}^{\text{ref}}$ is the diffusion coefficient in direction $i = \mathbb{R}$, T, L at reference conditions based on a gradient of c_b (mass of bound water per cell wall volume). The fitting coefficients a are given in Table 8.1.

i	R (radial)	T (tangential)	L (longitudinal)
$D_{b,i}^{\mathrm{ref}}$	1.036×10^{-12}	1.155×10^{-12}	3.893×10^{-12}
$a_{10,i}$	0.08897	0.24842	0.00910
$a_{11,i}$	0.86953	0.82168	1.04024
$a_{12,i}$	0.04272	0.02451	-0.04727
$a_{13,i}$	-0.00348	-0.09434	-0.00208
$a_{20,i}$	3296.19	3297.70	3296.43
$a_{21,i}$	-13304.7	-13310.5	-13305.6
$a_{22,i}$	20220.6	20229.0	20221.8
$a_{23,i}$	-13726.8	-13732.1	-13727.5
$a_{24,i}$	3515.65	3516.92	3515.82
$a_{30,i}$	0.38481	0.38566	0.36887
$a_{31,i}$	-1.84532	-1.85116	-1.73025
$a_{32,i}$	5.25007	5.26252	5.00110
$a_{33,i}$	-4.92452	-4.93665	-4.67909
$a_{34,i}$	2.13290	2.13758	2.03743

Table 8.1: Reference values $D_{b,i}^{\text{ref}} [\text{m}^2/\text{s}]$ and coefficients a_i for direction i = R, T, L, used in Eq. (8.5) for spruce clear wood and calculated based on results of the multiscale homogenization model.

The diffusion properties of water vapor in wood are more difficult to determine. As mentioned, the lumens of adjacent wood cells are interconnected by pits. When wood is dried from green conditions to conditions below the fiber saturation point, most of the pits get aspirated. But even in an aspirated state, the pits are much more permeable than the surrounding cell wall material. Thus the diffusion coefficients of water vapor are considerably affected by pit density, size, and aspiration state. These are hard to quantify, so that the water vapor diffusion coefficient in pure air is taken as basis and multiplied by empirical reduction factors ξ_i , $i \in [L, R, T]$, for each principal material direction [28]. These factors capture the different effects of the pits on water vapor diffusion in wood.

The diffusion coefficient for water vapor in wood can therefore be given as function of water vapor concentration and temperature as

$$D_{v,i} = \xi_i D_{\text{air}} = \xi_i \frac{0.026593 \,\overline{T}^{1.81}}{1013 + 13.529 \,\overline{c_v} \,\overline{T}} \quad [\text{m}^2/\text{s}], \quad i \in [\text{R}, \,\text{T}, \,\text{L}].$$
(8.7)

with

$$\xi_{\rm R} = 0.07, \quad \xi_{\rm T} = 0.05, \quad \xi_{\rm L} = 0.98.$$
 (8.8)

Therein, the diffusion coefficient of water vapor in air, D_{air} , was gained from combining a semi-empirical equation given by Schirmer [89] with the ideal gas law. $\bar{c}_v = c_v/(0.01 \text{ kg/m}^3)$ denotes the related water vapor concentration. The slightly higher value of ξ_{R} in radial direction than ξ_{T} in tangential direction arises from the influence of wood rays in this direction.

Chapter **9**

Numerical solution of the transient transport problem using FEM

As presented in Chapter 3, different sets of balance laws are needed to describe specific situations. For steady state moisture transport, steady state heat conduction, and the mechanical problem, single uncoupled balance laws are needed. Such problems can be solved analytically or numerically, e.g. by using a commercial finite element program and appropriate elements.

For the description of transient transport problems on a structural scale, three coupled, non-linear differential equations have to be solved in parallel. Unfortunately neither analytical solutions nor "ready-made" numerical solution are accessible for this problems. Hence, an own numerical solution is presented in this chapter in the framework of the finite element method. After deriving the weak form of the equations, their spatial discretization bases on interpolation function (depending on the chosen element type), while for the temporal discretization the backward Euler method is employed. The resulting set of discretized equations is then solved by means of a Newton-Raphson type iterative procedure.

For practical use, the model was implemented in the commercial finite element code ABAQUS. The most important parts of the according user element code are documented and described in the last section of this chapter.

9.1 Weak form of balance laws

Since an analytic solution of the three balance laws (3.30) to (3.32) cannot be achieved, they are discretized in space by means of the finite element method (FEM). For this

purpose, weak forms of the aforementioned equations are derived first [1]:

$$\int_{V} \delta c_b \left(\frac{\partial (c_b f_{\text{cwm}})}{\partial t} + \frac{\partial}{\partial \mathbf{x}} \cdot \mathbf{J}_b - \dot{c} \right) \mathrm{d}V = 0, \tag{9.1}$$

$$\int_{V} \delta c_{v} \left(\frac{\partial (c_{v} f_{\text{lum}})}{\partial t} + \frac{\partial}{\partial \mathbf{x}} \cdot \mathbf{J}_{v} + \dot{c} \right) \mathrm{d}V = 0, \tag{9.2}$$

$$\int_{V} \delta T \left(\frac{\partial(\rho e)}{\partial t} + \frac{\partial}{\partial \mathbf{x}} \cdot \mathbf{f} + \frac{\partial}{\partial \mathbf{x}} \cdot \mathbf{J}_{b} \,\overline{h}_{b} + \frac{\partial}{\partial \mathbf{x}} \cdot \mathbf{J}_{v} \,h_{v} + \dot{c} \left(h_{v} - h_{b}\right) \right) \mathrm{d}V = 0, \tag{9.3}$$

where δc_b , δc_v and δT are arbitrary variational fields, and V is an arbitrary volume. The variational fields have to fulfill the same boundary conditions as the actual fields c_b , c_v , and T, e.g. if $c_b = \bar{c}_b$ applies to one point of the surface of the body, then $c_b + \delta c_b = \bar{c}_b$ has to apply too, i.e. $\delta c_b = 0$ at the respective point.

In consideration of the product rule, Eqs. (9.1) to (9.3) can be rewritten as

$$\int_{V} \left[\delta c_b \, \frac{\partial (c_b \, f_{\text{cwm}})}{\partial t} + \frac{\partial}{\partial \mathbf{x}} \cdot (\delta c_b \, \mathbf{J}_b) - \mathbf{J}_b \cdot \frac{\partial \delta c_b}{\partial \mathbf{x}} - \delta c_b \, \dot{c} \right] \mathrm{d}V = 0, \tag{9.4}$$

$$\int_{V} \left[\delta c_v \, \frac{\partial (c_v \, f_{\text{lum}})}{\partial t} + \frac{\partial}{\partial \mathbf{x}} \cdot (\delta c_v \, \mathbf{J}_v) - \mathbf{J}_v \cdot \frac{\partial \delta c_v}{\partial \mathbf{x}} + \delta c_v \, \dot{c} \right] \mathrm{d}V = 0, \tag{9.5}$$

$$\int_{V} \left[\delta T \frac{\partial(\rho e)}{\partial t} + \frac{\partial}{\partial \mathbf{x}} \cdot (\delta T \mathbf{f}) - \frac{\partial \delta T}{\partial \mathbf{x}} \cdot \mathbf{f} + \frac{\partial}{\partial \mathbf{x}} \cdot (\delta T \mathbf{J}_{b}) \overline{h}_{b} - \frac{\partial \delta T}{\partial \mathbf{x}} \cdot \mathbf{J}_{b} \overline{h}_{b} + \frac{\partial}{\partial \mathbf{x}} \cdot (\delta T \mathbf{J}_{v}) h_{v} - \frac{\partial \delta T}{\partial \mathbf{x}} \cdot \mathbf{J}_{v} h_{v} + \delta T \dot{c} (h_{v} - h_{b}) \right] dV = 0. \quad (9.6)$$

Applying the divergence theorem, Eqs. (9.4) to (9.6) can be written as

$$\int_{V} \delta c_b \frac{\partial (c_b f_{\text{cwm}})}{\partial t} \, \mathrm{d}V - \int_{V} \frac{\partial \delta c_b}{\partial \mathbf{x}} \cdot \mathbf{J}_b \, \mathrm{d}V - \int_{V} \delta c_b \, \dot{c} \, \mathrm{d}V + \int_{S} \delta c_b \, \mathbf{n} \cdot \mathbf{J}_b \, \mathrm{d}S = 0, \quad (9.7)$$

$$\int_{V} \delta c_{v} \frac{\partial (c_{v} f_{\text{lum}})}{\partial t} \, \mathrm{d}V - \int_{V} \frac{\partial \delta c_{v}}{\partial \mathbf{x}} \cdot \mathbf{J}_{v} \, \mathrm{d}V + \int_{V} \delta c_{v} \, \dot{c} \, \mathrm{d}V + \int_{S} \delta c_{v} \, \mathbf{n} \cdot \mathbf{J}_{v} \, \mathrm{d}S = 0, \quad (9.8)$$

$$\int_{V} \delta T \frac{\partial(\rho e)}{\partial t} dV - \int_{V} \frac{\partial \delta T}{\partial \mathbf{x}} \cdot \mathbf{f} dV - \int_{V} \frac{\partial \delta T}{\partial \mathbf{x}} \cdot \mathbf{J}_{b} \overline{h}_{b} dV$$

$$- \int_{V} \frac{\partial \delta T}{\partial \mathbf{x}} \cdot \mathbf{J}_{v} h_{v} dV + \int_{V} \delta T \dot{c} (h_{v} - h_{b}) dV$$

$$+ \int_{S} \delta T \mathbf{n} \cdot \mathbf{f} dS + \int_{S} \delta T \mathbf{n} \cdot \mathbf{J}_{b} \overline{h}_{b} dS + \int_{S} \delta T \mathbf{n} \cdot \mathbf{J}_{v} h_{v} dS = 0, \qquad (9.9)$$

where S is the surface of the arbitrary volume V and **n** is the outward normal to S. Now, introducing the constitutive relations of Eqs. (3.15), (3.17), and (3.21), Eqs. (9.1) to (9.3) can be written as

$$\int_{V} \delta c_{b} \frac{\partial (c_{b} f_{cwm})}{\partial t} dV + \int_{V} \frac{\partial \delta c_{b}}{\partial \mathbf{x}} \cdot \mathbf{D}_{b} \cdot \frac{\partial c_{b}}{\partial \mathbf{x}} dV - \int_{V} \delta c_{b} \dot{c} dV - \int_{S} \delta c_{b} \phi_{b} dS = 0, \quad (9.10)$$

$$\int_{V} \delta c_{v} \frac{\partial (c_{v} f_{lum})}{\partial t} dV + \int_{V} \frac{\partial \delta c_{v}}{\partial \mathbf{x}} \cdot \mathbf{D}_{v} \cdot \frac{\partial c_{v}}{\partial \mathbf{x}} dV + \int_{V} \delta c_{v} \dot{c} dV - \int_{S} \delta c_{v} \phi_{v} dS = 0, \quad (9.11)$$

$$\int_{V} \delta T \rho c_{V} \frac{\partial T}{\partial t} dV + \int_{V} \frac{\partial \delta T}{\partial \mathbf{x}} \cdot \mathbf{K} \cdot \frac{\partial T}{\partial \mathbf{x}} dV + \int_{V} \frac{\partial \delta T}{\partial \mathbf{x}} \cdot \mathbf{D}_{b} \cdot \frac{\partial c_{b}}{\partial \mathbf{x}} \overline{h}_{b} dV$$

$$+ \int_{V} \frac{\partial \delta T}{\partial \mathbf{x}} \cdot \mathbf{D}_{v} \cdot \frac{\partial c_{v}}{\partial \mathbf{x}} h_{v} dV + \int_{V} \delta T \dot{c} (h_{v} - h_{b}) dV$$

$$- \int_{S} \delta T \phi_{T} dS - \int_{S} \delta T \phi_{b} \overline{h}_{b} dS - \int_{S} \delta T \phi_{v} h_{v} dS = 0, \quad (9.12)$$

where $\phi_b \stackrel{\text{def}}{=} -\mathbf{n} \cdot \mathbf{J}_b$, $\phi_v \stackrel{\text{def}}{=} -\mathbf{n} \cdot \mathbf{J}_b$ and $\phi_T \stackrel{\text{def}}{=} -\mathbf{n} \cdot \mathbf{f}$ are the bound water flux, the water vapor flux, and the heat flux, respectively, entering the body across S.

9.2 Spatial and temporal discretization

Following standard FEM, the unknown variables in the element domain are expressed in terms of their values at the element nodes by means of interpolation functions N:

$$\delta c_b = N^M \, \delta c_b^M, \qquad c_b = N^M \, c_b^M,$$

$$\delta c_v = N^N \, \delta c_v^N, \qquad c_v = N^N \, c_v^N,$$

$$\delta T = N^O \, \delta T^O, \qquad T = N^O \, T^O,$$

(9.13)

where discretized quantities are indicated by uppercase superscripts (for example c_b^N). Summation convention applies for these superscripts. Using Eqs. (9.13) in Eqs. (9.10) to (9.12) and considering that the variational fields δc_b , δc_v , and δT are arbitrarily chosen yields the discretized forms $F_{c_b}^M$, $F_{c_v}^N$, and F_T^O as

$$F_{c_b}^M = \int_V \mathbf{N}^M \frac{\partial (c_b f_{\text{cwm}})}{\partial t} \, \mathrm{d}V + \int_V \frac{\partial \mathbf{N}^M}{\partial \mathbf{x}} \cdot \mathbf{D}_b \cdot \frac{\partial c_b}{\partial \mathbf{x}} \, \mathrm{d}V - \int_V \mathbf{N}^M \dot{c} \, \mathrm{d}V - \int_S \mathbf{N}^M \phi_b \, \mathrm{d}S = 0,$$
(9.14)

$$F_{c_v}^N = \int_V \mathbf{N}^N \frac{\partial (c_v f_{\text{lum}})}{\partial t} \, \mathrm{d}V + \int_V \frac{\partial \mathbf{N}^N}{\partial \mathbf{x}} \cdot \mathbf{D}_v \cdot \frac{\partial c_v}{\partial \mathbf{x}} \, \mathrm{d}V + \int_V \mathbf{N}^N \dot{c} \, \mathrm{d}V - \int_S \mathbf{N}^N \phi_v \, \mathrm{d}S = 0,$$
(9.15)

$$F_T^O = \int_V \mathcal{N}^O \rho \, c_V \frac{\partial T}{\partial t} \, \mathrm{d}V + \int_V \frac{\partial \mathcal{N}^O}{\partial \mathbf{x}} \cdot \mathbf{K} \cdot \frac{\partial T}{\partial \mathbf{x}} \, \mathrm{d}V + \int_V \frac{\partial \mathcal{N}^O}{\partial \mathbf{x}} \cdot \mathbf{D}_b \cdot \frac{\partial c_b}{\partial \mathbf{x}} \, \overline{h}_b \, \mathrm{d}V + \int_V \frac{\partial \mathcal{N}^O}{\partial \mathbf{x}} \cdot \mathbf{D}_v \cdot \frac{\partial c_v}{\partial \mathbf{x}} \, h_v \, \mathrm{d}V + \int_V \mathcal{N}^O \, \dot{c} \, (h_v - h_b) \, \mathrm{d}V - \int_S \mathcal{N}^O \, \phi_T \, \mathrm{d}S - \int_S \mathcal{N}^O \, \phi_b \, \overline{h}_b \, \mathrm{d}S - \int_S \mathcal{N}^O \, \phi_v \, h_v \, \mathrm{d}S = 0,$$
(9.16)

For time integration, the backward Euler method is employed, yielding for time step Δt :

$$F_{c_b}^M = \frac{1}{\Delta t} \int_V \mathbf{N}^M \left(\left(c_b f_{\text{cwm}} \right) \Big|_{t+\Delta t} - \left(c_b f_{\text{cwm}} \right) \Big|_t \right) \, \mathrm{d}V + \int_V \frac{\partial \mathbf{N}^M}{\partial \mathbf{x}} \cdot \mathbf{D}_b \cdot \frac{\partial c_b}{\partial \mathbf{x}} \, \mathrm{d}V - \int_V \mathbf{N}^M \dot{c} \, \mathrm{d}V - \int_S \mathbf{N}^M \phi_b \, \mathrm{d}S = 0,$$
(9.17)

$$F_{c_v}^N = \frac{1}{\Delta t} \int_V \mathbf{N}^N \left(\left(c_v f_{\text{lum}} \right) \Big|_{t+\Delta t} - \left(c_v f_{\text{lum}} \right) \Big|_t \right) \, \mathrm{d}V + \int_V \frac{\partial \mathbf{N}^N}{\partial \mathbf{x}} \cdot \mathbf{D}_v \cdot \frac{\partial c_v}{\partial \mathbf{x}} \, \mathrm{d}V \\ + \int_V \mathbf{N}^N \dot{c} \, \mathrm{d}V - \int_S \mathbf{N}^N \phi_v \, \mathrm{d}S = 0,$$
(9.18)

$$F_T^O = \frac{1}{\Delta t} \int_V N^O \rho c_V \left(T \Big|_{t+\Delta t} - T \Big|_t \right) dV + \int_V \frac{\partial N^O}{\partial \mathbf{x}} \cdot \mathbf{K} \cdot \frac{\partial T}{\partial \mathbf{x}} dV + \int_V \frac{\partial N^O}{\partial \mathbf{x}} \cdot \mathbf{D}_b \cdot \frac{\partial c_b}{\partial \mathbf{x}} \overline{h}_b dV + \int_V \frac{\partial N^O}{\partial \mathbf{x}} \cdot \mathbf{D}_v \cdot \frac{\partial c_v}{\partial \mathbf{x}} h_v dV + \int_V N^O \dot{c} (h_v - h_b) dV - \int_S N^O \phi_T dS - \int_S N^O \phi_b \overline{h}_b dS - \int_S N^O \phi_v h_v dS = 0,$$
(9.19)

9.3 Solution method

The set of equations (9.17) - (9.19) is solved by means of a Newton-Raphson type iterative procedure [114]. The present case of three coupled differential equations results in the following system of equations for each integration point:

$$\begin{bmatrix} K_{c_bc_b}^{MP} & K_{c_bc_v}^{MQ} & K_{c_bT}^{MR} \\ K_{c_vc_b}^{NP} & K_{c_vc_v}^{NQ} & K_{c_vT}^{NR} \\ K_{c_vc_b}^{OP} & K_{c_vc_v}^{OQ} & K_{c_vT}^{NR} \\ \end{bmatrix}_{i} \begin{bmatrix} r_{c_b}^P \\ r_{c_v}^Q \\ r_{T}^R \\ i \end{bmatrix}_{i+1} \begin{bmatrix} \frac{\partial F_{c_b}^M}{\partial c_b^P} & \frac{\partial F_{c_b}^M}{\partial c_v^Q} & \frac{\partial F_{c_b}^M}{\partial T^R} \\ \frac{\partial F_{c_v}^P}{\partial c_b^P} & \frac{\partial F_{c_v}^O}{\partial c_v^Q} & \frac{\partial F_{c_v}^N}{\partial T^R} \\ \frac{\partial F_{T}^O}{\partial c_b^P} & \frac{\partial F_{C_v}^O}{\partial c_v^Q} & \frac{\partial F_{T}^O}{\partial T^R} \\ i \end{bmatrix}_{i+1} \begin{bmatrix} r_{c_b}^P \\ r_{c_v}^Q \\ r_{T}^P \\ i \end{bmatrix}_{i+1} \begin{bmatrix} r_{c_b}^P \\ r_{c_v}^Q \\ r_{T}^P \\ r_{T}^P \\ r_{T}^P \end{bmatrix}_{i+1} \begin{bmatrix} r_{c_b}^P \\ r_{c_v}^Q \\ r_{T}^P \\ r_{T}^P \\ r_{T}^P \end{bmatrix}_{i+1} \begin{bmatrix} r_{c_b}^P \\ r_{c_v}^Q \\ r_{C_v}^P \\ r_{T}^P \\ r_{T}^P \\ r_{T}^P \end{bmatrix}_{i+1} \begin{bmatrix} r_{c_b}^P \\ r_{c_v}^P \\ r_{c_v}^P \\ r_{T}^P \\ r_{T}^$$

where *i* is the iteration index. The components of the coefficient matrix are derived from variations of Eqs. (9.17) to (9.19) with respect to the three state variables $(c_b, c_v,$ and *T*) at time $t + \Delta t$. For uncoupled problems, the off-diagonal terms of the coefficient matrix vanish. The present case of strong connectivity between the state variables is characterized by non-zero off-diagonal terms. In the following, the components of the stiffness matrix are given. As regards boundary conditions, film boundary conditions for water vapor and temperature are considered [$\phi_v = k_v(c_v - c_v^0)$ and $\phi_T = k_T(T - T^0)$] for surface \bar{S} , see Section 3.4.

$$\begin{split} K_{c_bc_b}^{MP} &= \left. \frac{\partial F_{c_b}^M}{\partial c_b^P} \right|_{t+\Delta t} = \frac{1}{\Delta t} \int_V \mathbf{N}^M f_{\text{cwm}} \, \mathbf{N}^P \, \mathrm{d}V + \frac{1}{\Delta t} \int_V \mathbf{N}^M c_b \, \frac{\partial f_{\text{cwm}}(c_b)}{\partial c_b} \, \mathbf{N}^P \, \mathrm{d}V \\ &+ \int_V \frac{\partial \mathbf{N}^M}{\partial \mathbf{x}} \cdot \mathbf{D}_b \cdot \frac{\partial \mathbf{N}^P}{\partial \mathbf{x}} \, \mathrm{d}V \\ &+ \int_V \frac{\partial \mathbf{N}^M}{\partial \mathbf{x}} \cdot \frac{\partial \mathbf{D}_b(c_b, T)}{\partial c_b} \cdot \frac{\partial c_b}{\partial \mathbf{x}} \, \mathbf{N}^P \, \mathrm{d}V \\ &- \int_V \mathbf{N}^M \frac{\partial \dot{c}(c_b, c_v, T)}{\partial c_b} \, \mathbf{N}^P \, \mathrm{d}V \end{split}$$
(9.21)

$$K_{c_b c_v}^{MQ} = \left. \frac{\partial F_{c_b}^M}{\partial c_v^Q} \right|_{t+\Delta t} = -\int_V \mathcal{N}^M \frac{\partial \dot{c}(c_b, c_v, T)}{\partial c_v} \mathcal{N}^Q \, \mathrm{d}V \tag{9.22}$$

$$K_{c_bT}^{MR} = \left. \frac{\partial F_{c_b}^M}{\partial T^R} \right|_{t+\Delta t} = \int_V \frac{\partial \mathbf{N}^M}{\partial \mathbf{x}} \cdot \frac{\partial \mathbf{D}_b(c_b, T)}{\partial T} \cdot \frac{\partial c_b}{\partial \mathbf{x}} \mathbf{N}^R \,\mathrm{d}V \\ - \int_V \mathbf{N}^M \frac{\partial \dot{c}(c_b, c_v, T)}{\partial T} \,\mathbf{N}^R \,\mathrm{d}V$$
(9.23)

$$K_{c_v c_b}^{NP} = \left. \frac{\partial F_{c_v}^N}{\partial c_b^P} \right|_{t+\Delta t} = \frac{1}{\Delta t} \int_V N^N c_v \frac{\partial f_{\text{lum}}(c_b)}{\partial c_b} N^P \, \mathrm{d}V + \int_V \frac{\partial N^N}{\partial \mathbf{x}} \cdot \frac{\partial \mathbf{D}_v(c_b, c_v, T)}{\partial c_b} \cdot \frac{\partial c_b}{\partial \mathbf{x}} N^P \, \mathrm{d}V + \int_V N^N \frac{\partial \dot{c}(c_b, c_v, T)}{\partial c_b} N^P \, \mathrm{d}V$$
(9.24)

$$K_{c_v c_v}^{NQ} = \left. \frac{\partial F_{c_v}^N}{\partial c_v^Q} \right|_{t+\Delta t} = \frac{1}{\Delta t} \int_V N^N f_{\text{lum}} N^Q \, \mathrm{d}V + \int_V \frac{\partial N^N}{\partial \mathbf{x}} \cdot \mathbf{D}_v \cdot \frac{\partial N^Q}{\partial \mathbf{x}} \, \mathrm{d}V + \int_V \frac{\partial N^N}{\partial \mathbf{x}} \cdot \frac{\partial \mathbf{D}_v(c_b, c_v, T)}{\partial c_v} \cdot \frac{\partial c_v}{\partial \mathbf{x}} \, N^Q \, \mathrm{d}V + \int_V N^N \frac{\partial \dot{c}(c_b, c_v, T)}{\partial c_v} \, N^Q \, \mathrm{d}V - \int_{\bar{S}} N^N \, k_v \, N^Q \, \mathrm{d}S$$
(9.25)

$$K_{c_vT}^{NQ} = \frac{\partial F_{c_v}^N}{\partial T^R} \bigg|_{t+\Delta t} = \int_V \frac{\partial \mathbf{N}^N}{\partial \mathbf{x}} \cdot \frac{\partial \mathbf{D}_v(c_b, c_v, T)}{\partial T} \cdot \frac{\partial c_v}{\partial \mathbf{x}} \, \mathbf{N}^R \, \mathrm{d}V \\ + \int_V \mathbf{N}^N \frac{\partial \dot{c}(c_b, c_v, T)}{\partial T} \, \mathbf{N}^R \, \mathrm{d}V$$
(9.26)

$$\begin{split} K_{Tc_b}^{OP} &= \left. \frac{\partial F_T^O}{\partial c_b^P} \right|_{t+\Delta t} = \frac{1}{\Delta t} \int_V N^O \frac{\partial (\rho c_V)}{\partial c_b} \left(T \Big|_{t+\Delta t} - T \Big|_t \right) N^P \, dV \\ &+ \int_V \frac{\partial N^O}{\partial \mathbf{x}} \cdot \frac{\partial \mathbf{K}(c_b, T)}{\partial c_b} \cdot \frac{\partial T}{\partial \mathbf{x}} N^P \, dV \\ &+ \int_V \frac{\partial N^O}{\partial \mathbf{x}} \cdot \mathbf{D}_b \cdot \frac{\partial c_b}{\partial \mathbf{x}} N^P \frac{\partial \overline{h}_b(c_b, T)}{\partial c_b} \, dV \\ &+ \int_V \frac{\partial N^O}{\partial \mathbf{x}} \cdot \mathbf{D}_b \cdot \frac{\partial N^P}{\partial \mathbf{x}} \overline{h}_b \, dV \\ &+ \int_V \frac{\partial N^O}{\partial \mathbf{x}} \cdot \frac{\partial \mathbf{D}_b(c_b, T)}{\partial c_b} \cdot \frac{\partial c_b}{\partial \mathbf{x}} N^P \overline{h}_b \, dV \\ &+ \int_V \frac{\partial N^O}{\partial \mathbf{x}} \cdot \frac{\partial \mathbf{D}_b(c_b, T)}{\partial c_b} \cdot \frac{\partial c_b}{\partial \mathbf{x}} N^P h_b \, dV \\ &- \int_V N^O \, \dot{c} \, N^P \, \frac{\partial h_b(c_b, T)}{\partial c_b} \, dV \\ &+ \int_V N^O \frac{\partial \dot{c}(c_b, c_v, T)}{\partial c_b} \, N^P \, (h_v - h_b) \, dV \end{split} \tag{9.27}$$

$$K_{Tcv}^{OQ} = \frac{\partial F_T^O}{\partial c_v^Q} \Big|_{t+\Delta t} = \int_V \frac{\partial N^O}{\partial \mathbf{x}} \cdot \mathbf{D}_v \cdot \frac{\partial N^Q}{\partial \mathbf{x}} h_v \, \mathrm{d}V + \int_V \frac{\partial N^O}{\partial \mathbf{x}} \cdot \frac{\partial \mathbf{D}_v(c_b, c_v, T)}{\partial c_v} \cdot \frac{\partial c_v}{\partial \mathbf{x}} \, \mathrm{N}^Q \, h_v \, \mathrm{d}V + \int_V N^O \frac{\partial \dot{c}(c_b, c_v, T)}{\partial c_v} \, \mathrm{N}^Q \, (h_v - h_b) \, \mathrm{d}V - \int_{\bar{S}} \mathrm{N}^O \, k_v \, \mathrm{N}^Q \, h_v \, \mathrm{d}S$$
(9.28)

$$\begin{split} K_{TT}^{OR} &= \left. \frac{\partial F_T^O}{\partial T^R} \right|_{t+\Delta t} = \frac{1}{\Delta t} \int_V \mathbf{N}^O \rho \, c_V \, \mathbf{N}^R \, \mathrm{d}V \\ &+ \left. \frac{1}{\Delta t} \int_V \mathbf{N}^O \frac{\partial (\rho \, c_V)}{\partial T} \left(\left. T \right|_{t+\Delta t} - T \right|_t \right) \mathbf{N}^R \, \mathrm{d}V \\ &+ \int_V \frac{\partial \mathbf{N}^O}{\partial \mathbf{x}} \cdot \mathbf{K} \cdot \frac{\partial \mathbf{N}^R}{\partial \mathbf{x}} \, \mathrm{d}V \\ &+ \int_V \frac{\partial \mathbf{N}^O}{\partial \mathbf{x}} \cdot \frac{\partial \mathbf{K}(c_b, T)}{\partial T} \cdot \frac{\partial T}{\partial \mathbf{x}} \, \mathbf{N}^R \, \mathrm{d}V \\ &+ \int_V \frac{\partial \mathbf{N}^O}{\partial \mathbf{x}} \cdot \mathbf{D}_b \cdot \frac{\partial c_b}{\partial \mathbf{x}} \, \mathbf{N}^R \frac{\partial \overline{h}_b(c_b, T)}{\partial T} \, \mathrm{d}V \\ &+ \int_V \frac{\partial \mathbf{N}^O}{\partial \mathbf{x}} \cdot \frac{\partial \mathbf{D}_b(c_b, T)}{\partial T} \cdot \frac{\partial c_b}{\partial \mathbf{x}} \, \mathbf{N}^R \, \overline{h}_b \, \mathrm{d}V \\ &+ \int_V \frac{\partial \mathbf{N}^O}{\partial \mathbf{x}} \cdot \frac{\partial \mathbf{D}_v(c_b, c_v, T)}{\partial T} \cdot \frac{\partial c_b}{\partial \mathbf{x}} \, \mathbf{N}^R \, \overline{h}_b \, \mathrm{d}V \\ &+ \int_V \frac{\partial \mathbf{N}^O}{\partial \mathbf{x}} \cdot \mathbf{D}_v \cdot \frac{\partial c_v}{\partial \mathbf{x}} \, \mathbf{N}^R \frac{\partial h_v(T)}{\partial T} \, \mathrm{d}V \\ &+ \int_V \frac{\partial \mathbf{N}^O}{\partial \mathbf{x}} \cdot \frac{\partial \mathbf{D}_v(c_b, c_v, T)}{\partial T} \cdot \frac{\partial c_v}{\partial \mathbf{x}} \, \mathbf{N}^R \, h_v \, \mathrm{d}V \\ &+ \int_V \mathbf{N}^O \, \dot{c} \, \mathbf{N}^R \left[\frac{\partial h_v(T)}{\partial T} - \frac{\partial h_b(T)}{\partial T} \right] \, \mathrm{d}V \\ &+ \int_V \mathbf{N}^O \frac{\partial \dot{c}(c_b, c_v, T)}{\partial T} \, \mathbf{N}^R \, (h_v - h_b) \, \mathrm{d}V \\ &- \int_S \mathbf{N}^O k_T \, \mathbf{N}^R \, \mathrm{d}S \end{split}$$

The components of the coefficient matrix give rise to an unsymmetrical system of equations, requiring the use of a nonsymmetric matrix storage and solution scheme.

(9.29)

9.4 Implementation of the model in ABAQUS

The numerical solution scheme presented in this chapter was implemented as userelement in the commercial finite element code ABAQUS 6.9. The two-dimensional 4node element utilizes bilinear interpolation functions and includes all strong and weak couplings as given in Eq. (9.20). For each element the material orientation and the local density $\rho_{\rm cvm}^{\rm dry}$ have to be specified. Optionally, film boundary conditions may be used.

The strongest coupling arises from sorption, which is described by the microscale submodel [see Eq. (7.18)]. In the user-element, this sub-model is evaluated in each integration point at each time step for the actual bound water concentration c_b , water vapor concentration c_v , and temperature T.

9.4.1 User element subroutine UEL

In ABAQUS, the user element subroutine "UEL" enables the user to define an element. It offers complete control over the calculation, but on the other hand requires considerable coding in FORTRAN by the user. In order to solve the coupled system of equations as specified in Eq. (9.20), an according user element was developed. The general formulation of the main element subroutine can be easily adapted to different types of elements. The three degrees of freedom (DOF) or basic solution variables of the element are:

- DOF 11: bound water concentration c_b (CB) in [kg/m³],
- DOF 12: water vapor concentration c_v (CV) in $[10^{-4} \text{ kg/m}^3]$,
- DOF 13: thermodynamic temperature T (T) in [K].

The units were chosen to get similar orders of magnitude of the components of the coefficient matrix, which can be crucial for the stability of the calculation.

In general, several variables (RHS, AMATRX, SVARS, ENERGY) have to be defined in a user element subroutine. Which variables are relevant in a particular computation depends on the chosen solver and is controlled by so-called flags (LFLAGS). In order to carry out the computations, many variables are passed over to the subroutine by ABAQUS [1]. The most important of these variables are:

- NNODE is the user-defined number of nodes of the element, and NDOFEL is the number of degrees of freedom in the element.
- The array COORDS(I,J) contains the original coordinates of the element's nodes. For example, COORDS(2,4) is the second coordinate of the fourth node of the element
- The arrays U(I) and DU(I) contain the current estimates of the basic solution variables (concentrations and temperature) and their incremental values, respectively, at the nodes of the element at the end of the current increments. For example, for an element with four nodes (NNODE = 4) and three DOF (NDOFEL = 3), the array U is organized as follows:

9.4 Implementation of the model in ABAQUS

Variable number ${\tt I}$	Node number	Degree of freedom
1	1	1
2	1	2
3	1	3
4	2	1
5	2	2
6	2	3
7	3	1
8	3	2
9	3	3
10	4	1
11	4	2
12	4	3

- The variables TIME(1), TIME(2) and DTIME are the current values of step time, total time, and time increment, respectively.
- Several properties may be defined by the user in the input file of the calculation. They are passed into the subroutine in the vector PROPS. The number of userspecified properties is given by NPROPS.

In the header of the subroutine, first the number types and dimensions of all variables passed by ABAQUS are defined.

```
SUBROUTINE UEL (RHS, AMATRX, SVARS, ENERGY, NDOFEL, NRHS, NSVARS, PROPS,
1
          1 NPROPS, COORDS, MCRD, NNODE, U, dU, V, A, JTYPE, TIME, dTIME, KSTEP, KINC,
2
          2 JELEM, PARAMS, NDLOAD, JDLTYP, ADLMAG, PREDEF, NPREDF, LFLAGS,
3
4
          3 MLVARX, DDLMAG, MDLOAD, PNEWDT, JPROPS, NJPROP, PERIOD)
   С
\mathbf{5}
           IMPLICIT NONE
6
   С
\overline{7}
   С
           Variables passed by ABAQUS
8
           REAL*8 RHS, AMATRX, SVARS, ENERGY, PROPS, COORDS, U, DU, V, A, TIME, DTIME
9
10
           REAL*8 PARAMS, ADLMAG, PREDEF, MLVARX, DDLMAG, PNEWDT, PERIOD
           INTEGER NDOFEL, NRHS, NSVARS, NPROPS, MCRD, NNODE, JTYPE, KSTEP, KINC
11
12
           INTEGER JELEM, NDLOAD, JDLTYP, NPREDF, LFLAGS, MDLOAD, JPROPS, NJPROP
13
   С
           DIMENSION RHS(MLVARX,*), AMATRX(NDOFEL, NDOFEL), SVARS(NSVARS),
14
          1 ENERGY (24), PROPS (*), COORDS (MCRD, NNODE),
15
          2 U(NDOFEL), DU(MLVARX,*), V(NDOFEL), A(NDOFEL), TIME(2),
16
          3 PARAMS(2), JDLTYP(MDLOAD,*), ADLMAG(MDLOAD,*)
17
          4 DDLMAG(MDLOAD,*), PREDEF(2, NPREDF, NNODE), LFLAGS(*), JPROPS(*)
18
```

In addition to the variables given by ABAQUS, user-variables are defined. The nomenclature is in general equal to that in this thesis, in particular the additional variables are:

- CB, CV, and T are the bound water concentration, the water vapor concentration, and temperature at time $t + \Delta t$ in the integration point.
- CBold, CVold, and Told are the bound water concentration, the water vapor concentration, and temperature at time t in the integration point.
- Dcb and Dcv denote the diffusion tensors of bound water and water vapor, while K is the thermal conductivity tensor.

- RHO is the local oven-dry density.
- The enthalpies of bound water and water vapor are represented by Hb and Hv. Hbint is the integral enthalpy of bound water and RHOxcV the heat capacity per unit volume.
- ra denotes the outer radius of a wood cell, fcwm and flum are the volume fractions of cell wall material and lumens, respectively.
- EMC is the equilibrium moisture content as function of temperature and concentration of water vapor (which define the actual relative humidity), Dcwm is the diffusion coefficient of the cell wall material, and Cdot is the sorption rate term.
- XI, ETA, and ZETA are the isoparametric coordinates ξ , η , and ζ of the finite element. N are the according interpolation functions.
- As for numerical integration, GPX, GPY and GPZ are the isoparametric coordinates of the Gauss points, GWEI are the Gauss weights, detJACOBIAN is the determinant of the Jacobian matrix, and WE denotes the Gauss weight multiplied by the Jacobian determinant.
- SURFACE is a variable to be defined in the input file of a calculation, it is needed for using film boundary conditions. Each digit of the variable SURFACE represents one surface of the used element and is either 0 or 1. 1 implies that this element surface is on the boundary. For example, SURFACE= {0110} means that the surfaces 2 and 3 of this element exhibit film boundary conditions. For coding reasons, the string SURFACE is converted later into the vector S with the same content.
- The chosen iterative procedure requires many derivatives. In the subroutine a derivative of A with respect to B is represented by dA_dB.
- ROTMATRX is the three-dimensional rotation matrix, its transpose is denoted as ROTMATRX_T.
- I, J, KI, and KJ are used as indices. GP is the index of the actual Gauss point.
- Finally, VMV is a user defined function (see Section 9.4.4), calculating the product of a transposed vector times a square matrix times a vector.

```
Variables used in this Subroutine
   С
19
          REAL*8 RHO, SURFACE, GPX, GPY, GPZ, GWEI, GWE
20
          REAL*8 XI, ETA, ZETA
21
          REAL*8 N, dN_dX, dN_dY, dN_dZ, dN_dXI, dN_dETA, dN_dZETA
22
23
          REAL*8 dX_dXI,dX_dETA,dX_dZETA
          REAL*8 dY_dXI,dY_dETA,dY_dZETA
24
          REAL*8 dZ_dXI,dZ_dETA,dZ_dZETA
25
26
          REAL*8 detJACOBIAN,WE
          REAL*8 CB,CBold,dCB_dX,dCB_dY,dCB_dZ,dCB_dXvec
27
28
          REAL*8 CV,CVold,dCV_dX,dCV_dY,dCV_dZ,dCV_dXvec
          REAL*8 T, Told, dT_dX, dT_dY, dT_dZ, dT_dXvec
29
30
          REAL*8 Dcb,dDcb_dCB,dDcb_dCV,dDcb_dT
          REAL*8 Dcv,dDcv_dCB,dDcv_dCV,dDcv_dT
31
          REAL*8 K, dK_dCB, dK_dT
32
33
          REAL*8 RHOxcV, dRHOxcV_dCB, dRHOxcV_dT
          REAL*8 Hb, dHb_dCB, dHb_dT, Hv, dHv_dT
34
          REAL*8 Hbint,dHbint_dCB,dHbint_dT
35
          REAL*8 R2
36
```
```
REAL*8 fcwm,dfcwm_dC,flum,dflum_dCB,fcwmold,flumold
37
           REAL*8 EMC, dEMC_dCV, dEMC_dT
38
           REAL*8 Dcwm,dDcwm_dCB,dDcwm_dT
39
           REAL*8 Cdot,dCdot_dCB,dCdot_dCV,dCdot_dT
40
           REAL*8 dNI_dXvec,dNJ_dXvec,VMV
41
           REAL*8 K_T,T_0,K_CV,CV_0
42
43
           REAL*8 DS
44
           REAL *8 ROTMATRX, ROTMATRX_T
   С
45
46
           INTEGER NUMGP
           INTEGER I, J, GP, KI, KJ
47
           INTEGER S
48
    С
49
           DIMENSION GPX(20), GPY(20), GPZ(20)
50
51
           DIMENSION GWEI(20), GWE(20)
52
           DIMENSION N(NNODE), dN_dX(NNODE), dN_dY(NNODE), dN_dZ(NNODE)
           DIMENSION dN_dXI(NNODE), dN_dETA(NNODE), dN_dZETA(NNODE)
53
           DIMENSION dCB_dXvec(3), dCV_dXvec(3), dT_dXvec(3)
54
           \texttt{DIMENSION Dcb}(3,3), \texttt{dDcb}_\texttt{dCB}(3,3), \texttt{dDcb}_\texttt{dCV}(3,3), \texttt{dDcb}_\texttt{dT}(3,3)
55
           DIMENSION Dcv(3,3), dDcv_dCB(3,3), dDcv_dCV(3,3), dDcv_dT(3,3)
56
           DIMENSION K(3,3), dK_dCB(3,3), dK_dT(3,3)
57
           DIMENSION dNI_dXvec(3), dNJ_dXvec(3)
58
59
           DIMENSION S(6)
           DIMENSION ROTMATRX (3,3), ROTMATRX_T (3,3)
60
   С
61
62
   С
           Internal material property definition
   С
63
           SURFACE = PROPS(1)
64
65
           RHO = PROPS(2)
```

First, the right hand side vector RHS and the coefficient matrix AMATRX are initialized by setting all coefficients to zero.

```
C
          Initialization (NRHS=1)
66
67
   С
          DO 6 I=1,3*NNODE
68
69
              RHS(I,NRHS)=0D0
              DO 4 J=1,3*NNODE
70
71
                 AMATRX(J,I) = ODO
72
        4
              CONTINUE
        6 CONTINUE
73
```

As already mentioned, the variables to be defined are controlled by flags. A transient heat transfer analysis with a maximum allowable nodal temperature change given is indicated by LFLAGS(3) equaling 33. This procedure uses the requested backward time integration and a Newton-Raphson type iterative scheme [1].

74 IF (LFLAGS(1).EQ.33) THEN

In the next step, the isoparametric coordinates of the Gauss points and the according Gauss weights are determined. The do loop labeled by 300 is a loop through all Gauss points. At first the isoparametric coordinates, the real coordinates, the values of the interpolation functions in the element's nodes and all derivatives as well as the prefactors for numerical integration are determined.

```
75
   С
          Determination of Gauss point locations
   С
76
          CALL GSPT(GPX,GPY,GPZ,NUMGP)
77
   С
78
          Determination of Gauss weights
79
   С
80
   С
          CALL GSWT(GWEI,GWE)
81
   С
82
          DO 300 GP = 1, NUMGP
83
```

84	C Loop through Gauss points
85	XI = GPX(GP)
86	ETA = GPY(GP)
87	ZETA = GPZ(GP)
88	CALL DER(XI,ETA,ZETA,GPX,GPY,GPZ,GWEI,
89	1 N, dN_dX, dN_dY, dN_dZ, dN_dXI, dN_dETA, dN_dZETA,
90	2 dX_dXI,dX_dETA,dX_dZETA,
91	<pre>3 dY_dXI,dY_dETA,dY_dZETA,</pre>
92	4 dZ_dXI,dZ_dETA,dZ_dZETA,
93	5 detJACOBIAN, COORDS, MCRD, NNODE)
94	C
95	C Prefactor for numerical integration of parametric elements
96	WE = GWEI(GP) * det JACOBIAN

After their initialization, the values for bound water concentration, water vapor concentration, and temperature at the integration points are identified based on their values at the element's nodes. In addition, all their derivatives are derived and assembled in the vectors dCB_dXvec, dCV_dXvec, and dT_dXvec.

97		CB	=	0												
98		CBold	=	0												
99	С															
100		dCB_dX	=	0												
101		dCB_dY	=	0												
102		dCB_dZ	=	0												
103	С															
104		CV	=	0												
105		CVold	=	0												
106	С															
107		dCV_dX	=	0												
108		dCV_dY	=	0												
109		dCV_dZ	=	0												
110	С															
111		Т	=	0												
112		Told	=	0												
113	С															
114		dT_dX	=	0												
115		dT_dY	=	0												
116		dT_dZ	=	0												
117	C															
118		DO I=1,	ΝN	OD	E											
119		KI=3*	Ι-	2												
120		CB		=	U (K	(I)	*N((I)	+(СВ						
121		CBold		=	(U(ΚI) - d	1U ((K]	I,N	RHS))*	⊧N(I)+	СВо	ld
122		dCB_d	Х	=	U (K	(I)	*d1	I_d	LX ((I)	+dC	B_c	łХ			
123		dCB_d	Y	=	U (K	(I)	*d1	I_d	LY ((I)	+dC	B_I	ΡY			
124		dCB_d	Z	=	U (K	(I)	*d1	I_d	lZ ((I)	+dC	B_c	łΖ			
125	C															
126		KI=3*	Ι-	1												
127		CV		=	U(K	(I)	*N((I)	+(CV						
128		CVold		=	(U(KI) - (10 (K1	[, N	RHS)))	⊧N (I)+	CVo	ld
129		dCV_d	X	=	U (K	(1)	*d1	I_d		(I)	+dC	V_c	IX			
130		dCV_d	Y	=	U(K	(1)	*d1	[_d	LY ((1)	+dC	V_c	lΥ			
131	~	dCV_d	Z	=	U (K	(1)	*d1	1_c	IZ ((1)	+dC	V_c	12			
132	С		-													
133		KI=3*	T		/ -					_						
134		T		=	U(K	(1) (77	*N((L)	(+) ([' - •••	D II G	· · ·		- \ .		
135		Told		=	()((K I)-0	10 (KI.	L , N	RHS	k ((⊧N(1)+	Tol	d
136		dT_dX		=	U(K	(1)	*d1	1_0		(1)	+ d T	_dx				
137		dT_dY		=	U(K	(1) (T)	*dl	1_d		(1)	+dT	_d1	{			
138				=	U (K	(1)	* d I	1_c	LZ ((1)	+ d T	_d2	2			
139	a	END DU														
140	C	ACD JV		(4	>		CD	10								
141		ACD 4X	ec	(1)) =	d		αX	-							
142		ACB 4X-	ec	(2		- d	CB	α1 47	,							
143	C	acp_ava	eC	(3) =	- a	UB_	.uZ	•							
1 /1 /1																

145		dCV_dXvec(1)	=	dCV_dX
146		dCV_dXvec(2)	=	dCV_dY
147		dCV_dXvec(3)	=	dCV_dZ
148	С			
149		dT_dXvec(1)	=	dT_dX
150		dT_dXvec(2)	=	dT_dY
151		dT dXvec(3)	=	dT dZ

All material properties are defined in the separate subroutines MPROP_D, MPROP_K, and MPROP_THERMO as functions of bound water concentration, water vapor concentration, temperature and density. The according values were derived as described in Chapters 4 to 8 of this thesis.

152	CALL	MPROP_D(CB,CV,T,RHO,Dcb,dDcb_dCB,dDcb_dCV,dDcb_dT,
153	1	<pre>Dcv , dDcv_dCB , dDcv_dCV , dDcv_dT)</pre>
154	CALL	MPROP_K(CB,T,RHO,K,dK_dCB,dK_dT)
155	CALL	MPROP_THERMO(CB,CV,T,CBold,CVold,Told,RHO,
156	1	RHOxcV,dRHOxcV_dCB,dRHOxcV_dT,
157	2	Hb,dHb_dCB,dHb_dT,Hbint,dHbint_dCB,dHbint_dT,
158	3	Hv,dHv_dT)

The subroutine ROTMATRIX defines the local material orientation based on the coordinates of the actual Gauss point and the element's number. Thus individual samples with known fiber orientation may be defined. The following code lines rotate the material properties from local to global coordinates.

159		CALL ROTH	1 A I	RIX (COORDS, JELEM, ROTMATRX, ROTMATRX_T)
160	С			
161		Dcb	=	MATMUL (MATMUL (ROTMATRX, Dcb), ROTMATRX_T)
162		dDcb_dCB	=	MATMUL(MATMUL(ROTMATRX, dDcb_dCB), ROTMATRX_T)
163		dDcb_dT	=	MATMUL(MATMUL(ROTMATRX,dDcb_dT),ROTMATRX_T)
164		Dcv	=	MATMUL (MATMUL (ROTMATRX, Dcv), ROTMATRX_T)
165		dDcv_dCB	=	MATMUL(MATMUL(ROTMATRX, dDcv_dCB), ROTMATRX_T)
166		dDcv_dCV	=	MATMUL(MATMUL(ROTMATRX,dDcv_dVB),ROTMATRX_T)
167		dDcv_dT	=	MATMUL(MATMUL(ROTMATRX,dDcv_dT),ROTMATRX_T)
168		K	=	MATMUL (MATMUL (ROTMATRX,K), ROTMATRX_T)
169		dK_dCB	=	MATMUL (MATMUL (ROTMATRX, dK_dCB), ROTMATRX_T)
170		dK_dT	=	MATMUL(MATMUL(ROTMATRX, dK_dT), ROTMATRX_T)

The volume fractions of cell wall and lumen are defined in another subroutine as functions of density and bound water concentration:

```
      171
      CALL VOLUMEFRACTIONS (CB, CBold, RHO, fcwm, dfcwm_dCB, flum, dflum_dCB,

      172
      1

      172
      fcwmold, flumold)
```

In the next step, the sorption rate and its derivatives with respect to the basic solution variables are calculated. The average outer radius R2 of a tracheid cross section (see Fig 7.1) is derived based on an equation given by Perré [77] as function of density. The equilibrium moisture content EMC and the diffusion coefficient of the cell wall Dcwm are defined in additional subroutines as functions of bound water concentration, water vapor concentration, and temperature. As for the equilibrium moisture content EMC, it can be specified directly by a sorption isotherm or include sorption hysteresis in addition. This was done in this thesis based on the approach specified by Frandsen et al. [28], see Section 7.3.

The sorption rate Cdot then can be calculated based on Eq. (7.18).

```
173 C average outer radius of tracheid cross section
174 R2 = 0.5*(5D-5+(5.75D-5-3.75D-5*(RH0/1000)))
175 C
176 C Equilibrium moisture content and its derivatives wrt CV and T
```

```
CALL MPROP_EMC(CBold,CVold,Told,CV,T,EMC,dEMC_dCV,dEMC_dT)
177
    С
178
    С
          Diffusion coefficient of the cell wall in transversal direction
179
180
          CALL MPROP_DCWM (CB,T,Dcwm,dDcwm_dCB,dDcwm_dT)
    С
181
182
    C
          Sorption rate Cdot
          Cdot = (24*Dcwm*(EMC-CB)*flum**0.5*fcwm)/(R2**2*(5-7*flum**0.5
183
                -flum+3*flum**1.5))
184
         1
    С
185
186
    С
          Derivative of Cdot wrt CB
          dCdot_dCB = (24*(EMC-CB)*flum**0.5*fcwm)
187
                      /(R2**2*(5-7*flum**0.5-flum+3*flum**1.5))*dDcwm_dCB
188
         1
                      -(24*Dcwm*flum**0.5*fcwm)
189
         2
                      /(R2**2*(5-7*flum**0.5-flum+3*flum**1.5))
         3
190
191
         4
                      +(12*Dcwm*(EMC-CB)*(5+flum-6*flum**1.5)*fcwm)
192
         5
                      /(R2**2*(5*flum**0.25-7*flum**0.75-flum**1.25
                      +3*flum**1.75))*dflum_dCB
         6
193
194
         7
                      +(24*Dcwm*(EMC-CB)*flum**0.5)
         8
                      /(R2**2*(5-7*flum**0.5-flum+3*flum**1.5))*dfcwm_dCB
195
    C
196
          Derivative of Cdot wrt CV
197
    С
          dCdot_dCV = (24*Dcwm*flum**0.5*fcwm)/(R2**2*(5-7*flum**0.5
198
                      -flum+3*flum**1.5))*dEMC_dCV
199
         1
200
    С
          Derivative of Cdot wrt T
201
    С
202
          dCdot_dT
                   = (24*(EMC-CB)*flum**0.5*fcwm)
         1
                      /(R2**2*(5-7*flum**0.5-flum+3*flum**1.5))*dDcwm_dT
203
         2
                      +(24*Dcwm*flum**0.5)/(R2**2*(5-7*flum**0.5
204
205
         3
                      -flum+3*flum**1.5))*dEMC_dT
```

Finally, the solution vector RHS and the coefficient matrix AMATRX can be defined. They directly follow from Eqs. (9.17) to (9.19) and Eqs. (9.21) to (9.29), respectively.

```
C
           Loops over nodes
206
207
           DO I=1,NNODE
               dNI_dXvec(1) = dN_dX(I)
208
               dNI_dXvec(2) = dN_dY(I)
209
210
               dNI_dXvec(3) = dN_dZ(I)
211
     С
               --> RHS: Fcb (DOF 11)
               KI = 3 * I - 2
212
213
               RHS(KI,NRHS) = RHS(KI,NRHS)-WE*(0
                               +N(I)*(CB*fcwm-CBold*fcwmold)/dTIME
214
          1
                               +VMV(dNI_dXvec,Dcb,dCB_dXvec,3)
215
          2
          3
                               -N(I)*Cdot
216
          Х
                               )
217
218
               DO J=1,NNODE
                  dNJ_dXvec(1) = dN_dX(J)
219
                  dNJ_dXvec(2) = dN_dY(J)
220
                  dNJ_dXvec(3) = dN_dZ(J)
221
    С
                  --> AMATRX: derivative Fcb wrt CB
222
223
                  KJ = 3 * J - 2
                  AMATRX(KI,KJ) = AMATRX(KI,KJ)+WE*(0
224
                                   +N(I)*fcwm*N(J)/dTIME
          1
225
226
          2
                                   +N(I)*CB*dfcwm_dCB*N(J)/dTIME
          3
227
                                   +VMV(dNI_dXvec,Dcb,dNJ_dXvec,3)
                                   +VMV(dNI_dXvec,dDcb_dCB,dCB_dXvec,3)*N(J)
          4
228
229
          5
                                   -N(I)*dCdot_dCB*N(J)
230
          Х
                                    )
                  --> AMATRX: derivative Fcb wrt CV
    С
231
232
                  KJ = 3 * J - 1
                  AMATRX(KI,KJ) = AMATRX(KI,KJ)+WE*(0
233
234
          1
                                   -N(I)*dCdot_dCV*N(J)
                                   )
235
          Х
    С
                  --> AMATRX: derivative Fcb wrt T
236
237
                  K.I = 3 * .I
                  AMATRX(KI,KJ) = AMATRX(KI,KJ)+WE*(0
238
                                   +VMV(dNI_dXvec,dDcb_dT,dCB_dXvec,3)*N(J)
239
          1
          2
                                   -N(I)*dCdot_dT*N(J)
240
```

```
132
```

v

241		Х)
242			END DO
243	С		> RHS: Fcv (DOF 12)
244			KI=3*I-1
245			DHC(KI NDHC) = DHC(KI NDHC) - WE * (0)
240			M(T) = M(T) +
246		1	+N(I)*(CV*flum-CVold*flumold)/dllME
247		2	+VMV(dNI_dXvec,Dcv,dCV_dXvec,3)
248		3	+N(I)*Cdot*1D4
249		Х)
250			DO I=1 NNODE
200			A = A = A = A = A = A = A = A = A = A =
251			$dNJ_dAVec(1) = dN_dA(3)$
252			dNJ_dXvec(2) = dN_dY(J)
253			$dNJ_dXvec(3) = dN_dZ(J)$
254	С		> AMATRX: derivative Fcv wrt CB
255			KJ=3∗J−2
256			$\Delta M \Delta T R X (KT KI) = \Delta M \Delta T R X (KT KI) + W E * (0)$
250		1	$\frac{1}{1}$
257		1	
258		2	+ VMV(dN1_dXvec,dDcv_dCB,dCB_dXvec,3)*N(J)
259		3	$+N(I)*dCdot_dCB*N(J)*1D4$
260		Х)
261	С		> AMATRX: derivative Fcv wrt CV
262			KI=3*I-1
202			
263			AMAIRX(KI,KJ) = AMAIRX(KI,KJ)+WE*(0)
264		1	+N(I)*flum*N(J)/dTIME
265		2	+VMV(dNI_dXvec,Dcv,dNJ_dXvec,3)
266		3	+VMV(dNI_dXvec,dDcv_dCV,dCV_dXvec,3)*N(J)
267		4	+N(I)*dCdot dCV*N(I)*1D4
201		v	
208	a	л	
269	C		> AMAIRA: derivative FCV wrt 1
270			KJ = 3 * J
271			AMATRX(KI,KJ) = AMATRX(KI,KJ)+WE*(O
272		1	+VMV(dNI_dXvec,dDcv_dT,dCV_dXvec,3)*N(J)
273		2	+N(I)*dCdot dT*N(J)*1D4
274		y v	
214		А	
275	-		
276	С		> RHS: Ft (DOF 13)
277			KI=3*I
278			RHS(KI,NRHS) = RHS(KI,NRHS)-WE*(0
279		1	+N(I)*RHOxcV*(T-Told)/dTIME
280		2	+VMV(dNI dXvec K dT dXvec 3)
200		2	tunu (ani du co, Dab d'Ob d'uno 2) tubint
281		3	
282		4	+VMV(dN1_dXvec,Dcv,dCV_dXvec,3)*Hv
283		5	+N(I)*Cdot*(Hv-Hb)
284		Х)
285			DO J=1.NNODE
286			$dN \downarrow dV = c(1) = dN dX(1)$
280			
287			$dNJ_dXVec(2) = dN_dY(J)$
288			$dNJ_dXvec(3) = dN_dZ(3)$
289	С		> AMATRX: derivative Ft wrt CB
290			KJ=3∗J−2
291			AMATRX(KI,KJ) = AMATRX(KI,KJ) + WE * (0)
202		1	+N(T) * dRHOYCV dCR * (T-Told) * N(T)/dTIME
202		- -	
293		2	+ VMV (aNI_aXVec, aK_aCB, aI_aXVec, 3) * N(J)
294		3	+ VMV (dN1_dXvec, Dcb, dCB_dXvec, 3) *N (J) * dHbint_dCB
295		4	+VMV(dNI_dXvec,Dcb,dNJ_dXvec,3)*Hbint
296		5	+VMV(dNI_dXvec,dDcb_dCB,dCB_dXvec,3)*N(J)*Hbint
297		6	+VMV(dNI_dXvec,dDcv_dCB,dCV_dXvec,3)*N(J)*Hv
298		7	-N(I)*Cdot*N(J)*dHb dCB
200		8	$+\mathbb{N}(\mathbf{I}) * d\mathbf{C} d_{\mathbf{C}} + d\mathbf{C} \mathbf{D} * (\mathbf{I}) * (\mathbf{u}_{\mathbf{C}} - \mathbf{u}_{\mathbf{L}})$
499		v)
300	~	Y	
301	С		> AMATRX: derivative Ft wrt CV
302			KJ=3*J-1
303			AMATRX(KI,KJ) = AMATRX(KI,KJ)+WE*(0
304		1	+VMV(dNI dXvec.Dcv.dNJ dXvec.3)*Hv
305		2	+VMV(dNI dXvec dDcv dCV dCV dXvec $3) * N(1) * Hv$
200		2	$\pm \mathbb{N}(\mathbf{T}) + d\mathbf{C}d_{\mathbf{C}} + d\mathbf{C}\mathbf{U} + \mathbb{N}(\mathbf{T}) + (\mathbf{U}_{\mathbf{C}} - \mathbf{U}_{\mathbf{C}})$
300		J	+ M (Ι) * αύαυς_αυν * M (J) * (Πν - ΠD)
307	~	Y	
308	C		> AMATRX: derivative Ft wrt T

309	ł	(J=3*J
310	I	AMATRX(KI,KJ) = AMATRX(KI,KJ)+WE*(O
311	1	$+N(I)*RHOxcV_dT*N(J)/dTIME$
312	2	+N(I)*dRHOxcV_dT*(T-Told)*N(J)/dTIME
313	3	+VMV(dNI_dXvec,K,dNJ_dXvec,3)
314	4	+VMV(dNI_dXvec,dK_dT,dT_dXvec,3)*N(J)
315	5	+VMV(dNI_dXvec,Dcb,dCB_dXvec,3)*N(J)*dHbint_dT
316	6	+VMV(dNI_dXvec,dDcb_dT,dCB_dXvec,3)*N(J)*Hbint
317	7	+VMV(dNI_dXvec,Dcv,dCV_dXvec,3)*N(J)*dHv_dT
318	8	+VMV(dNI_dXvec,dDcv_dT,dCV_dXvec,3)*N(J)*Hv
319	9	$+N(I)*Cdot*N(J)*(dHv_dT-dHb_dT)$
320	0	$+N(I)*dCdot_dT*N(J)*(Hv-Hb)$
321	Х)
322	END	DO
323	END DO	
324	C	
325	300 CONTINU	JE

As mentioned, the user element allows for using film boundary conditions. As shown in Eqs. (9.17) to (9.19) and Eqs. (9.21) to (9.29), film boundary conditions result in additional terms in the solution vector RHS and the coefficient matrix AMATRX of the actual element. The following code for the film boundary conditions is explicitly formulated for a two-dimensional bilinear element. This element exhibits four faces, for each face the film boundary conditions have to be specified separately.

First it is checked if particular faces of the element exhibit film boundary conditions. Afterwards the digits of the integer SURFACE are assigned to the components of vector S. The properties of the film boundary conditions, i.e. the film boundary coefficients for water vapor and energy, k_v and k_T , respectively, as well as the ambient climate specified by the ambient water vapor concentration $c_{v,0}$ and the ambient temperature T_0 are defined in the additional subroutine FILM_BC.

```
Check if element is at the boundary (else no film boundary conditions)
    С
326
           IF (SURFACE .NE. ODO) THEN
327
    С
           Extract digits of PROPS(1)
328
           S(1) = INT(SURFACE/1000)
329
           S(2) = INT(SURFACE/100) - 10 * S(1)
330
           S(3) = INT(SURFACE/10) - 10 * S(2) - 100 * S(1)
331
           S(4) = INT(SURFACE/1) - 10 * S(3) - 100 * S(2) - 1000 * S(1)
332
333
    С
           Assign film properties
           CALL FILM_BC(K_T,T_0,K_CV,CV_0)
334
```

Next the film boundary conditions for surfaces No. 1 ($\eta = -1$), No. 2 ($\xi = +1$), No. 3 ($\eta = +1$), and No. 4 ($\xi = -1$) are calculated (for the definition of the surfaces see Fig. 9.1 on page 138). After checking if the particular surface exhibits film boundary conditions, the additional terms in the solution vector **RHS** and the coefficient matrix **AMATRX** are calculated. Numerical integration of the surface integral is performed with two Gauss points on the respective surface.

```
Film boundary conditions, surface No. 1 (ETA = -1)
    С
335
    С
336
337
           IF (S(1) .EQ. 1) THEN
    С
           Loop through surface Gauss points
338
339
           DO GP = 1,2
               XI
                    = GPY(GP)
340
               ETA = -1
341
               ZETA = 0
342
               CALL DER(XI, ETA, ZETA, GPX, GPY, GPZ, GWEI,
343
                         N, dN_dX, dN_dY, dN_dZ, dN_dXI, dN_dETA, dN_dZETA,
344
          1
          2
                         dX_dXI, dX_dETA, dX_dZETA,
345
          3
                         dY_dXI, dY_dETA, dY_dZETA,
346
                         dZ_dXI,dZ_dETA,dZ_dZETA,
347
          4
```

134

```
detJACOBIAN, COORDS, MCRD, NNODE)
          5
348
349
    С
               Determination of state variables in the surface Gauss point
350
               T = 0
               CV = 0
351
               DO I=1,NNODE
352
                  KI = 3*I-1
CV = U(KI)*N(I)+CV
353
354
                  KI = 3 * I
355
                  T = U(KI) * N(I) + T
356
357
               END DO
               Prefactor for numerical integration for parametric elements
    С
358
               DS = GWE(GP) * SQRT(dX_dXI * dX_dXI + dY_dXI * dY_dXI)
359
    С
               Loops over Nodes
360
               DO I=1,NNODE
361
    С
               --> RHS: Fcv (DOF 12)
362
363
                  KI=3*I-1
                  RHS(KI,NRHS) = RHS(KI,NRHS)
364
365
          1
                                  -DS*N(I)*K_CV*(CV-CV_0)
                  DO J=1,NNODE
366
    С
                      --> AMATRX: derivative Fcv wrt CV
367
                      KJ = 3 * J - 1
368
                      AMATRX(KI,KJ) = AMATRX(KI,KJ)
369
                                       -DS*N(I)*K_CV*N(J)
370
          1
                  END DO
371
    С
               --> RHS: Ft (DOF 13)
372
373
                  KI = 3 * I
374
                  RHS(KI,NRHS) = RHS(KI,NRHS)
                                  -DS*N(I)*K_T*(T-T_0)
375
          1
376
                  DO J=1,NNODE
                     --> AMATRX: derivative Ft wrt T
    С
377
378
                     KJ = 3 * J
                      AMATRX(KI,KJ) = AMATRX(KI,KJ)
379
          1
                                       -DS*N(I)*K_T*N(J)
380
381
                  END DO
              END DO
382
           END DO
383
384
           END IF
    С
385
           Film boundary conditions, surface No. 2 (XI = +1)
386
    С
387
    С
           IF (S(2) .EQ. 1) THEN
388
    С
389
           Loop through surface Gauss points
           DO GP = 1,2
390
              ΧТ
                    = 1
391
               ETA = GPY(GP)
392
               ZETA = 0
393
               CALL DER(XI, ETA, ZETA, GPX, GPY, GPZ, GWEI,
394
395
          1
                         N, dN_dX, dN_dY, dN_dZ, dN_dXI, dN_dETA, dN_dZETA,
          2
                         dX_dXI, dX_dETA, dX_dZETA,
396
397
          3
                         dY_dXI, dY_dETA, dY_dZETA,
398
          4
                         dZ_dXI,dZ_dETA,dZ_dZETA,
                         detJACOBIAN, COORDS, MCRD, NNODE)
          5
399
    С
               Determination of state variables in the surface Gauss point
400
401
               T = 0
               CV = 0
402
               DO I=1,NNODE
403
                  KI = 3 * I - 1
404
                  CV = U(KI) * N(I) + CV
405
                  KI = 3 * I
406
                  T = U(KI) * N(I) + T
407
408
               END DO
    С
               Prefactor for numerical integration for parametric elements
409
               DS = GWE(GP)*SQRT(dX_dETA*dX_dETA + dY_dETA*dY_dETA)
410
               Loops over Nodes
411
    С
               DO I=1,NNODE
412
    С
413
               --> RHS: Fcv (DOF 12)
                  KI=3*I-1
414
                  RHS(KI,NRHS) = RHS(KI,NRHS)
415
```

```
-DS*N(I)*K_CV*(CV-CV_0)
416
          1
                  DO J=1,NNODE
417
    С
                      --> AMATRX: derivative Fcv wrt CV
418
419
                      K.I = 3 * .I - 1
                      AMATRX(KI,KJ) = AMATRX(KI,KJ)
420
                                        -DS*N(I)*K_CV*N(J)
421
          1
                  END DO
422
               --> RHS: Ft (DOF 13)
423
    С
                  KI=3*I
424
425
                  RHS(KI,NRHS) = RHS(KI,NRHS)
                                   -DS*N(I)*K_T*(T-T_0)
426
          1
                  DO J=1,NNODE
427
    С
                      --> AMATRX: derivative Ft wrt T
428
                      KJ = 3 * J
429
                      AMATRX(KI,KJ) = AMATRX(KI,KJ)
430
431
          1
                                       -DS*N(I)*K_T*N(J)
                  END DO
432
433
               END DO
           END DO
434
           END TF
435
    С
436
    С
           Film boundary conditions cont Surface No. 3 (ETA = +1)
437
438
    С
           IF (S(3) .EQ. 1) THEN
439
    С
           Loop through surface Gauss points
440
441
           DO GP = 1, 2
               XI = GPY(GP)
442
               ETA = 1
443
444
               ZETA = 0
               CALL DER (XI, ETA, ZETA, GPX, GPY, GPZ, GWEI,
445
446
          1
                         N, dN_dX, dN_dY, dN_dZ, dN_dXI, dN_dETA, dN_dZETA,
                         dX_dXI, dX_dETA, dX_dZETA,
447
          2
          3
                         dY_dXI, dY_dETA, dY_dZETA,
448
449
          4
                         dZ_dXI,dZ_dETA,dZ_dZETA,
          5
                         det JACOBIAN, COORDS, MCRD, NNODE)
450
    С
               Determination of state variables in the surface Gauss point
451
               T = 0
452
               CV = 0
453
               DO I=1,NNODE
454
                  KI = 3*I-1
455
                  CV = U(KI) * N(I) + CV
456
457
                  KI = 3 * I
                  T = U(KI) * N(I) + T
458
               END DO
459
460
    С
               Prefactor for numerical integration for parametric elements
               DS = GWE(GP) * SQRT(dX_dXI * dX_dXI + dY_dXI * dY_dXI)
461
462
    С
               Loops over Nodes
463
               DO I=1,NNODE
    С
               --> RHS: Fcv (DOF 12)
464
465
                  KI=3∗I-1
                  RHS(KI,NRHS) = RHS(KI,NRHS)
466
                                   -DS*N(I)*K_CV*(CV-CV_0)
467
          1
468
                  DO J=1,NNODE
                      --> AMATRX: derivative Fcv wrt CV
469
    С
470
                      K.I = 3 * .I - 1
                      AMATRX(KI,KJ) = AMATRX(KI,KJ)
471
                                       -DS*N(I)*K_CV*N(J)
          1
472
473
                  END DO
               --> RHS: Ft (DOF 13)
474
    С
                  KI=3*I
475
476
                  RHS(KI,NRHS) = RHS(KI,NRHS)
          1
                                   -DS * N(I) * K_T * (T - T_0)
477
478
                  DO J=1,NNODE
                      --> AMATRX: derivative Ft wrt T
     С
479
                      K.I = 3 * .I
480
                      AMATRX(KI,KJ) = AMATRX(KI,KJ)
481
                                       -DS*N(I)*K_T*N(J)
482
          1
                  END DO
483
```

136

```
END DO
484
485
           END DO
           END IF
486
487
    С
    С
           Film boundary conditions cont Surface No. 4 (XI = -1)
488
    С
489
           IF (S(4) .EQ. 1) THEN
490
    С
           Loop through surface Gauss points
491
           DO GP = 1,2
492
              XI
493
                    = -1
               ETA = GPY(GP)
494
               ZETA = 0
495
496
               CALL DER(XI, ETA, ZETA, GPX, GPY, GPZ, GWEI,
                         N, dN_dX, dN_dY, dN_dZ, dN_dXI, dN_dETA, dN_dZETA,
497
          1
498
          2
                         dX_dXI,dX_dETA,dX_dZETA,
499
          3
                         dY_dXI, dY_dETA, dY_dZETA,
                         dZ_dXI,dZ_dETA,dZ_dZETA,
          4
500
501
          5
                         detJACOBIAN, COORDS, MCRD, NNODE)
    С
              Determination of state variables in the surface Gauss point
502
              T = 0
503
               CV = 0
504
               DO I=1,NNODE
505
                  KI = 3 * I - 1
506
                  CV = U(KI) * N(I) + CV
507
                  KI = 3 * I
508
                  T = U(KI) * N(I) + T
509
              END DO
510
    С
               Prefactor for numerical integration for parametric elements
511
512
               DS = GWE(GP)*SQRT(dX_dETA*dX_dETA + dY_dETA*dY_dETA)
    С
               Loops over Nodes
513
514
               DO I=1,NNODE
    С
               --> RHS: Fcv (DOF 12)
515
                  KI=3∗I-1
516
517
                  RHS(KI,NRHS) = RHS(KI,NRHS)
                                  -DS*N(I)*K_CV*(CV-CV_0)
518
          1
                  DO J=1,NNODE
519
520
    С
                     --> AMATRX: derivative Fcv wrt CV
                     KJ=3*J-1
521
                     AMATRX(KI,KJ) = AMATRX(KI,KJ)
522
                                      -DS*N(I)*K_CV*N(J)
523
          1
                  END DO
524
               --> RHS: Ft (DOF 13)
525
    С
                  KI = 3 * I
526
                  RHS(KI,NRHS) = RHS(KI,NRHS)
527
528
          1
                                  -DS*N(I)*K_T*(T-T_0)
                  DO J=1,NNODE
529
    С
                     --> AMATRX: derivative Ft wrt T
530
531
                     KJ = 3 * J
                     AMATRX(KI,KJ) = AMATRX(KI,KJ)
532
533
          1
                                      -DS*N(I)*K_T*N(J)
                  END DO
534
              END DO
535
536
           END DO
           END IF
537
    С
538
539
           END IF
540
```

Finally, the user element subroutine is concluded by:

541	END IF
542	RETURN
543	END

9.4.2 Subroutines defining the element type

Except for the film boundary conditions, the user element subroutine presented in the previous subsection is generally formulated in terms of the element type. It might be adapted for one-, two-, or three-dimensional elements with arbitrary isoparametric interpolation functions. In this thesis, a two-dimensional 4-node element with linear interpolation functions was chosen (a preliminary two-dimensional 8-node element with quadratic interpolation function showed numerical instabilities for some model configurations). The according numberings of nodes, integration points and faces are given in Fig. 9.1.



Figure 9.1: Two-dimensional bilinear element: Numbering of nodes (\circ), integration points (\times), and faces. ξ and η are the parameterized local coordinates.

The number of Gauss points and their isoparametric coordinates [66] are specified in subroutine GSPT:

```
SUBROUTINE GSPT(GPX,GPY,GPZ,NUMGP)
1
    С
2
           REAL*8 GPX, GPY, GPZ, R
3
4
           INTEGER NUMGP
5
    С
           DIMENSION GPX(4), GPY(4), GPZ(4)
6
    С
7
           NUMGP = 4
8
    С
9
           R=1/SQRT(3)
10
    С
11
12
           GPX(1) = -R
           GPX(2) = R
13
14
           GPX(3) = R
           GPX(4) = -R
15
    С
16
           GPY(1) = -R
17
           GPY(2) = -R
18
           GPY(3) = R
19
20
           GPY(4) = R
    С
21
           GPZ(1) = 0
22
           GPZ(2) = 0
23
           GPZ(3) = 0
24
           GPZ(4) = 0
25
    С
26
           RETURN
27
           END
28
```

The according Gauss weights GWEI for each Gauss point [66] (in this case equal to 1) are defined in subroutine GSWT.

```
SUBROUTINE GSWT(GWEI,GWE)
1
    С
\mathbf{2}
3
            REAL*8 GWEI,GWE
4
            INTEGER I, J, GP
    С
\mathbf{5}
            DIMENSION GWEI(4), GWE(2)
6
    С
7
            GWE(1) = 1
8
            GWE(2) = 1
9
10
            DO 10 I=1,2
             DO 10 J=1,2
11
                GP=(I-1) *2+J
12
13
                 GWEI(GP) = GWE(I) * GWE(J)
            CONTINUE
     10
14
15
            RETURN
16
            END
```

The subroutine DER defines the value of the interpolation functions N_i (one for each node *i*) and their derivatives with respect to the three spatial directions x, y, and z for given isoparametric coordinates ξ , η , and ζ . In addition, the determinant of the Jacobian matrix is defined. For the chosen two-dimensional bilinear element, subroutine DER reads as:

```
SUBROUTINE DER (XI, ETA, ZETA, GPX, GPY, GPZ, GWEI,
 1
                             N, dN_dX, dN_dY, dN_dZ, dN_dXI, dN_dETA, dN_dZETA,
          1
2
 3
          2
                             dX_dXI, dX_dETA, dX_dZETA,
 4
          3
                             dY_dXI, dY_dETA, dY_dZETA,
          4
                             dZ_dXI,dZ_dETA,dZ_dZETA,
 5
 6
          5
                             detJACOBIAN, COORDS, MCRD, NNODE)
    С
 7
 8
           REAL*8 XI, ETA, ZETA,
           REAL*8 GPX,GPY,GPZ,GWEI
9
           REAL*8 dX_dXI,dX_dETA,dX_dZETA
10
11
           REAL*8 dY_dXI,dY_dETA,dY_dZETA
12
           REAL*8 dZ_dXI,dZ_dETA,dZ_dZETA
           REAL*8 N
13
14
           REAL*8 dN_dX,dN_dY,dN_dZ
           REAL*8 dN_dXI, dN_dETA, dN_dZETA
15
           REAL*8 detJACOBIAN
16
           REAL*8 COORDS
17
           INTEGER MCRD, NNODE
18
19
           INTEGER I,J
    С
20
           DIMENSION N(NNODE)
21
           DIMENSION dN_dX(NNODE), dN_dY(NNODE), dN_dZ(NNODE)
22
           DIMENSION dN_dXI(NNODE), dN_dETA(NNODE), dN_dZETA(NNODE)
23
           DIMENSION COORDS (MCRD, NNODE)
24
    С
25
    С
           Interpolation functions
26
27
    С
           N(1) = 0.25*(1-XI)*(1-ETA)
28
           N(2) = 0.25 * (1 + XI) * (1 - ETA)
29
30
           N(3) = 0.25*(1+XI)*(1+ETA)
31
           N(4) = 0.25*(1-XI)*(1+ETA)
    С
32
33
    С
           Derivatives wrt to XI
    С
34
           dN_dXI(1) = -0.25*(1 - ETA)
35
           dN_dXI(2) = 0.25*(1-ETA)
36
           \frac{dN_{dXI}(3)}{dN_{dXI}(4)} = 0.25*(1+ETA)
\frac{dN_{dXI}(4)}{dN_{dXI}(4)} = -0.25*(1+ETA)
37
38
   С
39
40
   C
           Derivatives wrt to ETA
    С
41
```

```
dN_dETA(1) = -0.25*(1-XI)
42
43
          dN_dETA(2) = -0.25*(1+XI)
          dN_dETA(3) = 0.25*(1+XI)
44
45
          dN_dETA(4) = 0.25*(1-XI)
   С
46
   С
          Derivatives wrt to ZETA
47
48
   С
          dN_dZETA(1) = 0
49
          dN_dZETA(2) = 0
50
          dN_dZETA(3) = 0
51
          dN_dZETA(4) = 0
52
   С
53
          dX_dXI
                   = 0
54
                   = 0
          dX dETA
55
          dX_dZETA = 0
56
57
          dY_dXI
                   = 0
                   = 0
          dY dETA
58
59
          dY_dZETA = 0
                   = 0
          dZ_dXI
60
                  = 0
61
          dZ dETA
          dZ_dZETA = 0
62
63
          DO 3 I=1,NNODE
64
            dX_dXI = dX_dXI + COORDS(1,I)*dN_dXI(I)
65
            dX_dETA = dX_dETA + COORDS(1,I)*dN_dETA(I)
66
            dY_dXI = dY_dXI + COORDS(2,I)*dN_dXI(I)
67
            dY_dETA = dY_dETA + COORDS(2,I)*dN_dETA(I)
68
        3 CONTINUE
69
70
   С
   С
          Calculation of the Jacobian determinant
71
72
   С
          detJACOBIAN = (dX_dXI*dY_dETA-dX_dETA*dY_dXI)
73
   С
74
75
   С
          Derivatives of N wrt to X, Y, and Z
   С
76
          DO 5 I=1, NNODE
77
            dN_dX(I) = (dN_dXI(I) *dY_dETA-dN_dETA(I)*dY_dXI )/detJACOBIAN
78
            dN_dY(I) = (dN_dETA(I)*dX_dXI -dN_dXI(I) *dX_dETA)/detJACOBIAN
79
80
            dN_dZ(I) = 0
        5 CONTINUE
81
          RETURN
82
83
          END
```

9.4.3 Subroutine for equilibrium moisture content including hysteresis

For the calculation of the equilibrium moisture content the approach given by Frandsen (see Section 7.3) is used. The nomenclature in the Fortran code is again equal to that used in this thesis. In the header of the subroutine, the number types of all used variables are defined.

```
SUBROUTINE MPROP_EMC (CBold, CVold, Told, CV, T, EMC, dEMC_dCV, dEMC_dT)
1
2
   С
          REAL*8 CBold, CVold, Told
3
4
          REAL*8 tau,dtau_dT
          REAL*8 CV,T,CVsat,dCVsat_dT
\mathbf{5}
          REAL*8 PHI, dPHI_dT, dPHI_dCV
6
          REAL*8 EMC, dEMC_dCV, dEMC_dT
7
8
          REAL*8 F1a,F2a,F3a,F1d,F2d,F3d,D1,D2,Q1,Q2
          REAL*8 PHI0, MC0, SO
9
10
          REAL*8 PHIa0, PHId0, MCa0, MCd0
          REAL*8 MCa, MCd, dMCa_dPHI, dMCd_dPHI
11
12
          REAL*8 S,dS_dPHI,dEMC_dPHI
```

In the next step, the parameters defining the sorption boundary curves and the shape of the scanning curve are defined. The values are equal to that in Chapter 11.

```
Hailwood-Horrobin adsorption boundary curve
   С
13
          F1a = 1.234
14
          F2a = 10.214
15
          F3a = -8.122
16
   С
17
   С
          Hailwood-Horrobin desorption boundary curve
18
19
          F1d = 2.456
          F2d = 10.311
20
          F3d = -8.791
21
   С
22
   С
          Shape parameter
23
24
          D1 = -1.50
          D2 = 0.85
25
```

The conditions at time t are used as initial conditions for the calculation. The initial relative humidity PHIO is calculated by relating the water vapor concentration at time t, CVold, to the according saturation vapor concentration CVsat. The latter is calculated based on an empirical equation given in [90] using the temperature at time t, Told.

```
tau = 1 - Told / 647.14
26
   С
27
   С
          Saturation vapor concentration for given temperature [kg/m^3]
28
          CVsat = (47806.90077/Told)*EXP((647.14/Told)*
29
30
         1
                   (-7.85823*tau
                                   +1.83991*tau**1.5
                    -11.7811*tau**3+22.6705*tau**3.5
31
         2
         3
                    -15.9393*tau**4+1.77516*tau**7.5))
32
   С
33
   С
          Relative humidity [1]
34
          PHIO = CVold/(CVsat*1D4)
35
```

The initial moisture content MCO is gained by dividing the bound water concentration at time t, CBold, by the dry density of the cellwall (1530 kg/m³). Based on the initial relative humidity PHIO, the initial boundary values for adsorption and desorption are calculated by use of the Hailwood-Horrobin isotherm [see Eq. (7.26)].

```
36 MC0 = CBold/1530
37 C
38 MCa0 = PHI0/(F1a+F2a*PHI0+F3a*PHI0**2)
39 C
40 MCd0 = PHI0/(F1d+F2d*PHI0+F3d*PHI0**2)
```

The initial parameter S0 follows from Eq. (7.20).

41 C Parameter S0 42 S0 = (MC0-MCa0)/(MCd0-MCa0)

Now the initial state (PHIO,SO) is defined, thus the auxiliary variables Q1, Q2, PHIaO, and PHIdO are calculated as given in Eqs. (7.22) to (7.25).

```
Q1 = -(LOG(LOG(2)) - LOG(LOG(2-SO))) /
43
         1
                 (LOG(LOG(2))-LOG(LOG(2-SO))-D1)
44
45
   С
          Q_2 = -(LOG(LOG(2)) - LOG(LOG(1+S0))) /
46
                 (LOG(LOG(2)) - LOG(LOG(1+S0)) - D1)
47
         1
   С
48
          PHIa0 = PHIO*((D2*PHIO)**Q1)
49
          PHId0 = 1-(1-PHI0)*(D2*(1-PHI0))**Q2
50
```

Also for the actual state (time $t + \Delta t$) the relative humidity PHI is calculated. In addition, its derivatives with respect to water vapor concentration and temperature, dPHI_dCV and dPHI_dT, are computed.

```
tau = 1 - T / 647.14
51
          dtau_dT = -1/647.14
52
   С
53
          Saturation vapor concentration for given temperature [kg/m^3]
54
   С
          CVsat = (47806.90077/T) * EXP((647.14/T) *
55
         1
                   (-7.85823*tau +1.83991*tau**1.5
56
57
         2
                    -11.7811*tau**3+22.6705*tau**3.5
58
         3
                    -15.9393*tau**4+1.77516*tau**7.5))
   С
59
60
   С
          Derivative of CVsat wrt T
          dCVsat_dT = (-1/T) * CVsat + CVsat * (
61
62
         1
                        (-647.14/T**2)*
                        (-7.85823*tau
                                        +1.83991*tau**1.5
63
         2
                         -11.7811*tau**3+22.6705*tau**3.5
         3
64
65
         4
                         -15.9393*tau**4+1.77516*tau**7.5)
66
         5
                        +(647.14/T)*dtau_dT*
                                           +1.83991*1.5*tau**0.5
                         (-7.85823)
67
         6
68
                         -11.7811*3*tau**2+22.6705*3.5*tau**2.5
         7
         8
                         -15.9393*4*tau**3+1.77516*7.5*tau**6.5))
69
   С
70
          Relative humidity [1]
71
   С
          PHI = CV/(CVsat*1D4)
72
73
          dPHI_dCV = 1/(CVsat*1D4)
          dPHI_dT = -CV/(CVsat**2*1D4)*dCVsat_dT
74
```

The actual scanning curve parameter S then directly follows from Eq. (7.21). Further, its derivative with respect to relative humidity, dS_dPHI, is derived.

```
IF (PHI.GE.PHIO) THEN
75
            IF (SO.EQ.O) THEN
76
              S = 0
77
              dS_dPHI = 0
78
            ELSE
79
              S = -1+2**(((1-PHI)/(1-PHId0))**(D1/(LOG(D2*(1-PHId0)))))
80
              dS_dPHI = -1*2**(((1-PHI)/(1-PHId0))**(D1/(LOG(D2*(1-PHId0))))))
81
                        *(((1-PHI)/(1-PHId0))**(D1/(LOG(D2*(1-PHId0)))))
82
         1
83
         2
                        *(D1/(LOG(D2*(1-PHId0))))*LOG(2)/(1-PHI)
            END IF
84
85
          ELSE
            IF (SO.EQ.1) THEN
86
87
              S = 1
              dS_dPHI = 0
88
            ELSE
89
              S = 2-2**((PHI/PHIa0)**(D1/(LOG(D2*PHIa0))))
90
91
              dS_dPHI = -1*2**((PHI/PHIaO)**(D1/(LOG(D2*PHIaO))))
                        *((PHI/PHIa0)**(D1/(LOG(D2*PHIa0))))
         1
92
93
         2
                        *(D1/(LOG(D2*PHIa0)))*LOG(2)/PHI
            END IF
94
          END IF
95
```

The values of the boundary curves based on the actual relative humidity are again calculated using the Hailwood-Horrobin isotherms.

```
      96
      MCa = PHI/(F1a+F2a*PHI+F3a*PHI**2)

      97
      dMCa_dPHI = (F1a-F3a*PHI**2)/((F1a+F2a*PHI+F3a*PHI**2)**2)

      98
      C

      99
      MCd = RH/(F1d+F2d*PHI+F3d*PHI**2)

      100
      dMCd_dPHI = (F1d-F3d*PHI**2)/((F1d+F2d*PHI+F3d*PHI**2)**2)
```

Finally, the actual equilibrium moisture content, EMC follows from Eq. (7.19). In addition, the solution scheme of the user element requires the derivatives of EMC with respect to water vapor concentration and temperature, they are calculated using the chain rule of differentiation.

102 EMC = 1530*((MCd-MCa)*S+MCa) 103 C

142

```
Derivative of EMC wrt CV
    С
104
105
            dEMC_dCV = 1530*dPHI_dCV*(dMCa_dPHI
                                         +dMCd_dPHI *S+MCd*dS_dPHI
106
           1
                                          -dMCa_dPHI*S-MCa*dS_dPHI)
107
          2
108
    С
           Derivative of EMC wrt T
dEMC_dT = 1530*dPHI_dT*(dMCa_dPHI
109
     С
110
           1
                                       +dMCd_dPHI *S+MCd *dS_dPHI
111
          2
                                       -dMCa_dPHI *S-MCa *dS_dPHI)
112
    С
113
            RETURN
114
            END
115
```

9.4.4 Additional functions

As mentioned before, the user subroutine often requires the calculation of the scalar product of a transposed vector VEC1, a square matrix MATRX, and another vector VEC2. For simplification, an according function was generally defined, with M as the number of rows / columns of VEC1, MATRX, and VEC2.

```
REAL*8 FUNCTION VMV(VEC1,MATRX,VEC2,M)
 1
    С
\mathbf{2}
           REAL*8 VEC1, MATRX, VEC2
3
           INTEGER I, J, M
4
    С
 \mathbf{5}
           DIMENSION VEC1(M), VEC2(M)
6
           DIMENSION MATRX(M,M)
7
    С
 8
           VMV = 0
9
10
           DO I=1,M
11
              DO J=1,M
                 VMV = VMV + VEC1(J)*MATRX(J,I)*VEC2(I)
12
             END DO
13
           END DO
14
           RETURN
15
16
           END
```

Chapter 10

Validation I: Improved cup method

In the previous chapters of this thesis, a mathematical description of the hygro-thermomechanical material wood was developed, the therein needed material properties were derived using multiscale approaches, and a numerical solution for transient transport problems was given in the framework of the finite element method. However, what is still missing is the validation and verification of the whole model. The aim of modeling work is to provide predictions of the behavior of materials and structures in real situations – therefore validation is based on comparisons of model predicted values with according experimental results at a structural scale.

Under special conditions, e.g. steady state diffusion processes as specified in Eq. 3.29, processes are largely defined by one material property, e.g. by the diffusion coefficient. For such cases, a suitable validation may rest on a direct comparison of model predicted material properties and according measurements, as it was done in Chapters 4, 5, and 6 of this thesis for thermal conductivity, steady state moisture diffusivity, and viscoelastic properties of wood.

In contrast, transient transport processes cannot be suitably captured by solely one material property, rather they are governed by at least three coupled differential equations [see Eq. (3.30) to (3.32)] including several material properties. Therefore the validation of the according model rests on the prediction of whole processes.

A first validation of the model is based on experimental results gained with the improved cup method. The aim was to design a special test setup that excludes possible uncertainties regarding the diffusion properties coming from microstructural characteristics. Thus, only longitudinal moisture transport was permitted in the test, because in this direction the transport routes of both water vapor and bound water are clearly defined as a consequence of the longitudinally aligned cell lumens. For modeling purposes, the diffusion coefficient of water vapor in air (see e.g. [89]) can be directly used in the model without consideration of reduction factors. A further reason why to look at longitudinal moisture transport is that for this direction the most significant differences between steady-state and transient moisture transport behavior are observed.

10.1 Introduction

Water vapor transport in air is significantly faster than bound water transport in the wood cell wall. As a consequence of the longitudinally aligned cell lumens, the moisture flow in the longitudinal direction consists of two diffusion processes in parallel.

When the longitudinal dimension of a wood sample approaches zero, the influence of the tapered ends of the tracheids vanishes and the longitudinal diffusion coefficient of water vapor in cell lumens $D_{v,L}$ reaches its limit given by the moisture diffusion coefficient of pure air D_{air} . Thus Eqs. (3.30) and (3.31) reduce for thin specimens in good approximation to [48]

$$\frac{\partial(c_b f_{\rm cwm})}{\partial t} \approx \dot{c},\tag{10.1}$$

$$\frac{\partial (c_v f_{\text{lum}})}{\partial t} \approx \frac{\partial}{\partial z} \left(D_{\text{air}} \frac{\partial c_v}{\partial z} \right) - \dot{c}, \qquad (10.2)$$

where z is the longitudinal material direction. In sorption tests without cup, only the changes in bound water concentration in terms of total weight increase or decrease are measured. With the modified method the relative humidities on both sides of the specimens are measured in addition, constituting important additional values for model validation.

The primary aim of the improved cup method was the direct measurement of the sorption rate \dot{c} , assuming that Eqs. (10.1) and (10.2) are the complete description of transient transport processes. But, as shown in Chapter 3, also an energy balance is needed in addition. Therefore the sorption rate could not be suitably correlated to the difference in concentrations alone (see Publication 6 in the appendix of this thesis). In the following section, the corresponding test setup and testing procedure are described in detail.

10.2 Materials and methods

10.2.1 Sample preparation

Norway Spruce (*Picea abies*) specimens were cut with a circular saw, with the smallest dimension in the longitudinal material direction (referred to as thickness in Table 10.1). To fit into the cups, the dimensions of the specimens were approximately $65 \times 40 \text{ mm}^2$. Specimens contained no growth irregularities (knots, reaction wood).

The specimen preparation with a saw resulted in a rough-textured surface with macrofibrils sticking out. Removal of these fibrils by sanding resulted in filling the lumens with residue, this would be unacceptable for later tests that require open lumens. Thus, the rough surfaces were left untreated, and no further processing of the specimens was performed.

To fit into a diffusion cup, the wood specimens were centered in a plastic ring. A layer of silicone kept the specimen in place and, together with aluminum foil, ensured a vapor



Figure 10.1: Specimen for the improved cup method.

Specimen No.	thickness [mm]	area $[mm^2]$	$volume$ $[mm^3]$	dry mass [g]	dry density $[g/cm^3]$
1	1.55	2801	4341	1.952	0.450
2	1.55	2548	3950	1.763	0.446
3	2.70	2365	7512	2.841	0.445
4	2.76	2794	7711	3.419	0.443
5	3.06	2827	8651	3.830	0.443
6	3.45	2462	8493	3.730	0.439
7	6.45	2768	17853	7.864	0.440
8	6.42	2831	18178	7.987	0.439

Table 10.1: Dimensions and densities of test specimens

tight seal (see Figs. 10.1 and 10.2). Dimensions and densities of the eight specimens analyzed in this study are given in Table 10.1.

Further, the sorption isotherm, which is similar for all samples, was determined as

$$MC = \frac{\varphi}{4.182 + 9.342\,\varphi - 10.319\,\varphi^2}, \qquad 5\,\% < \varphi < 80\,\%. \tag{10.3}$$

10.2.2 Method

A diffusion cup is a cylindrical metal container, consisting of a cup and a screw cap with a circular opening (see Fig. 10.2). Between these two parts, a specimen is fitted with one surface inward and the other outward the cup. Rubber ring-sealings assure the tightness of the whole assembly ensuring transport into or out of the cup through the specimen without leakage. In a traditional cup test a salt solution is used to establish a specific constant humidity inside the cup, while the outside of the cup is exposed to a different constant humidity. Assuming validity of a transport law like Fick's first law of diffusion [see Eq. (3.16)], a steady state diffusion coefficient can be calculated (as done e.g. by Comstock [11]). The concentration gradient $\partial c/\partial \mathbf{x}$ is the concentration difference between inside and outside of the cup divided by the thickness of the specimen, while the flux \mathbf{J} is the mass loss of the specimen per time divided by the specimen area. The mass loss per time is usually determined by repeated weighing of the whole cup.

The improved cup method aimed at direct measurement of the sorption process inside wood during a transient transport process. In contrast to the common cup method, the "improved" cup contains no salt solution but a small data logger (Tinytag Ultra 2 TGU-4500) in order to monitor the course of relative humidity and temperature inside the cup during the sorption test. This setup (see Fig. 10.2) allows for a more precise measurement and experimental analysis of the transport and sorption processes in wood.



Figure 10.2: Test setup of the improved cup method and according model representation.

In addition to the eight cups with specimens, two reference cups were prepared. In order to test the configuration for tightness, one reference cup contained a completely sealed dummy specimen. The second reference cup was open to check the sorption behavior of the rubber sealing and the data logger and to monitor the climatic conditions inside the chamber. In all assembled cups, a special vacuum grease (Apiezon[®] M Grease) on the rubber sealings was used to assure complete impermeability.

All cups were assembled and placed in one climate cabinet at a temperature of $+20^{\circ}$ C and a relative humidity (φ) of 4 %, which corresponds to an equilibrium moisture content below 1 %. Equilibrium was reached within 2 days. Subsequently, relative humidity inside the chamber was changed in three steps:

- step 1: from 4.0 to 22.5 %,
- step 2: from 22.5 to 41.0 %,
- step 3: from 41.0 to 76.5 %.

Each step was a uniform change of relative humidity in the climate cabinet. Establishing a new humidity in the cabinet took between 1000 and 1500 seconds. Afterwards this humidity was kept constant until all specimens reached mass constancy. A PC-logger recorded temperature and relative humidity in the climate chamber and a fan ensured uniform water vapor concentration. By periodic weighing the cups, the mass changes of the specimens were determined. The moisture content for each specimen was calculated as the fractional actual mass over dry mass of the specimen.

10.3 Boundary conditions

Diffusion inside wood is not the only transport process in wetting and drying of a wood specimen. Depending on air velocity, humidity in air, temperature, and surface roughness of the specimen, there is a boundary layer of air between the specimen surface and the moving air in the surrounding atmosphere – an additional barrier, in which moisture and energy are transported both by diffusion and convection. Particularly for specimens with relatively fast internal transport (as it is the case for the longitudinal material direction in wood), this boundary layer essentially influences the results and has to be accounted for.

Also in cup tests a boundary layer of air between the specimen surface and the moving air in the chamber slows down water transport to the specimen. Such an additional resistance can be suitably expressed in terms of a film boundary condition [see Eq. (3.26)]:

$$\bar{\mathbf{J}}_v = -k_v \left(c_{v,s} - c_{v,a} \right) \,\mathbf{n}.\tag{10.4}$$

where $\bar{\mathbf{J}}_v$ is the flux through the surface, $c_{v,s}$ is the surface vapor concentration, $c_{v,a}$ is the ambient vapor concentration, and k_v is a mass transfer coefficient. It strongly depends on air velocity and temperature, but only very slightly on relative humidity [27]. Therefore a simple test was developed, where the surface flux and both vapor concentrations are exactly known. For direct measurement of this mass transfer coefficient a standard



Figure 10.3: Test assembly for the measurement of boundary conditions

diffusion cup as used for the improved cup method was assembled without a specimen but completely filled with water (see Fig. 10.3). This cup was placed in the climate chamber. Above the water surface the relative humidity φ_s naturally is 100%. The climate chamber was set to a relative humidity of $\varphi_a = 30\%$ and a temperature of 19.6 °C, resulting in water evaporation from the water surface and therefore a loss of mass of the water-filled cup. The transport of water vapor from the water surface towards the climate chamber due to the air flow in the climate chamber is the only transport process in this system, inside water certainly no mass transport occurs. Thus the mass transfer coefficient can be calculated directly – the surface flux is the mass change with time $(\Delta m/\Delta t)$ divided by the free water surface area A:

$$\bar{\mathbf{J}}_v \cdot \mathbf{n} = \frac{\Delta m}{A \cdot \Delta t}.\tag{10.5}$$

Consequently, rearrang Eq. (10.4) yields

$$k_v = -\frac{\Delta m}{A \cdot \Delta t} \cdot \frac{1}{c_{v,s} - c_{v,a}} = -\frac{\Delta m}{A \cdot \Delta t} \cdot \frac{1}{c_{v,\text{sat}}(\varphi_s - \varphi_a)},\tag{10.6}$$

where $c_{v,\text{sat}}$ denotes the saturated water vapor concentration (for numerical values see e.g. [33]). For the actual temperature of 19.6 °C $c_{v,\text{sat}}$ is 0.0168 kg/m³. The mass change with time was measured by continuously weighing, to be $\Delta m/\Delta t = -1.43 \cdot 10^{-7} \text{ kg/s}$, the free water surface area A was 0.005 m^2 . Using these numerical values in Eq. (10.6) yields

$$k_v = 0.00243 \,\mathrm{m/s.} \tag{10.7}$$

For illustration, this value can be divided by the actual diffusion coefficient of air, resulting in an equivalent layer thickness of stagnant air of 1.02 cm. The corresponding heat transfer coefficient k_T was calculated [27] as $k_T = 2.655 \text{ W/(m^2 K)}$. Heat transfer towards the sample surface pointing inwards the cup was negligibly small due to the stagnant air inside the cup.

10.4 Comparison of experimental results and model predictions

The test can be suitably represented by a one-dimensional model shown in Fig. 10.2. The coupled system of equations for the heat and moisture transport in the sample was solved using the user-defined finite element explained in Chapter 9. Validation of the model was then based on comparing model predictions for two characteristics and their change over time with corresponding test results: the average moisture content \overline{MC} of the sample and the relative humidity φ_i inside the cup. The latter was calculated based on water vapor concentration c_v and temperature T on the lower face of the sample.

Figures 10.4 to 10.11 show the results of the comparison for all samples and the three different humidity steps. Therein, moisture contents and relative humidities predicted by the model are plotted against time, together with the corresponding experimental results. The courses of moisture content and relative humidity are predicted very well for all thicknesses and different steps in relative humidity.

The obviously good agreement of experimental and computational results for different configurations shows the plausibility of the underlying assumptions in the model. This is an important step towards real prediction of transport processes in wood, which in the end should be applicable also to non-tested conditions.

10.5 Summary

This chapter covers the development and the application of an improved cup method. It aims to investigate moisture transport in the longitudinal material direction of wood below the fiber saturation point in thin specimens, where water is transported primarily by water vapor diffusion, while changes in bound water content are governed by sorption and not by bound water transport. The experiment was conducted on eight specimens of Norway Spruce with different thicknesses and for three steps in relative humidity. Finally a first validation of the modeling approach developed in this thesis is presented, based on comparison of simulation results to independent experimental results. The gained results are very promising and verify the validity of the underlying theory.



Step 1: relative humidity $4.0 \rightarrow 22.5 \%$

Figure 10.4: Comparison of experimental results and corresponding model predictions: Average moisture content \overline{MC} and internal relative humidity φ_i over time for sample No. 1: Norway spruce, thickness $\ell = 1.55 \text{ mm}$, dry density $\rho_{\text{wood}}^{\text{dry}} = 450 \text{ kg/m}^3$.



Figure 10.5: Comparison of experimental results and corresponding model predictions: Average moisture content \overline{MC} and internal relative humidity φ_i over time for sample No. 2: Norway spruce, thickness $\ell = 1.55 \text{ mm}$, dry density $\rho_{\text{wood}}^{\text{dry}} = 446 \text{ kg/m}^3$.



Step 1: relative humidity $4.0 \rightarrow 22.5 \%$

Figure 10.6: Comparison of experimental results and corresponding model predictions: Average moisture content \overline{MC} and internal relative humidity φ_i over time for sample No. 3: Norway spruce, thickness $\ell = 2.70 \text{ mm}$, dry density $\rho_{\text{wood}}^{\text{dry}} = 445 \text{ kg/m}^3$.



Step 1: relative humidity $4.0 \rightarrow 22.5\,\%$

Figure 10.7: Comparison of experimental results and corresponding model predictions: Average moisture content \overline{MC} and internal relative humidity φ_i over time for sample No. 4: Norway spruce, thickness $\ell = 2.76 \text{ mm}$, dry density $\rho_{\text{wood}}^{\text{dry}} = 443 \text{ kg/m}^3$.



Step 1: relative humidity $4.0 \rightarrow 22.5 \%$

Figure 10.8: Comparison of experimental results and corresponding model predictions: Average moisture content \overline{MC} and internal relative humidity φ_i over time for sample No. 5: Norway spruce, thickness $\ell = 3.06 \text{ mm}$, dry density $\rho_{\text{wood}}^{\text{dry}} = 443 \text{ kg/m}^3$.



Step 1: relative humidity $4.0 \rightarrow 22.5\,\%$

Figure 10.9: Comparison of experimental results and corresponding model predictions: Average moisture content \overline{MC} and internal relative humidity φ_i over time for sample No. 6: Norway spruce, thickness $\ell = 3.45 \text{ mm}$, dry density $\rho_{\text{wood}}^{\text{dry}} = 439 \text{ kg/m}^3$.



Step 1: relative humidity $4.0 \rightarrow 22.5 \%$

Figure 10.10: Comparison of experimental results and corresponding model predictions: Average moisture content \overline{MC} and internal relative humidity φ_i over time for sample No. 7: Norway spruce, thickness $\ell = 6.45 \text{ mm}$, dry density $\rho_{\text{wood}}^{\text{dry}} = 440 \text{ kg/m}^3$.



Figure 10.11: Comparison of experimental results and corresponding model predictions: Average moisture content \overline{MC} and internal relative humidity φ_i over time for sample No. 8: Norway spruce, thickness $\ell = 6.42 \text{ mm}$, dry density $\rho_{\text{wood}}^{\text{dry}} = 439 \text{ kg/m}^3$.

Chapter **11**

Validation II: Multinuclear resonance imaging

In the previous chapter, a first validation of the transient transport model could be given. It is based on a comparison of the overall mass increase and the relative humidity on the surface of the samples, but no detailed information about the process inside the sample was accessible. However, especially such information is of great importance in order to check the suitability of a model for transport process. In this chapter an additional experimental study is presented that allows for a non-destructive determination of bound water distributions inside a sample using proton magnetic resonance imaging. The gained experimental results then served as basis for an enhanced validation of the transient transport model.

11.1 Introduction

The classical way to examine transient moisture transport in wood are sorption experiments (see e.g. Section 10 or the work of Wadsö [109]), in which the mass increase of a sample is recorded over time. Gradients inside the sample can only be determined by cutting the sample into thin slices [49] in a destructive way. Therefore in the last years several non-destructive experimental methods were developed, based on X-ray computer tomography (CT) [85], neutron imaging [67], and proton magnetic resonance imaging (MRI) [17]. These methods allow for a continuous monitoring of moisture profiles during transient changes of the environmental conditions. In the experimental study presented in this chapter MRI was used because of its non-invasive nature, spatial selectivity, short measurement times, and quantitative response. Moisture distributions were measured in three samples with different orientations of the principal material directions subjected to three steps in relative humidity. Thus it was possible to validate the model by comparing model predictions not only to the overall mass increase of a sample but also to experimentally derived moisture profiles inside the sample at different time instances.

11.2 Materials and methods

The tests aimed at measuring the moisture transport behavior of wood in its three principal material directions. The three cylindrical samples – one for each material direction – used in the experiment were cut from one board of Norway spruce with dimensions and mean densities as given in Table 11.1.

		iable iiii bailip	bie properties	
No.	direction	$\rho_{\rm wood}^{\rm dry} \ [\rm kg/m^3]$	height [mm]	diameter [mm]
1	radial	378.84	21.6	7.90
2	tangential	431.86	20.2	7.90
3	longitudinal	401.30	23.3	7.88

Table 11.1: Sample properties

The samples were sealed with adhesive tape on all sides except for one which was exposed to controlled climatic conditions. This results in a one-dimensional moisture transport process with a moisture flux normal to the unsealed surface. The prepared wood samples were assembled in an NMR tube as shown in Fig. 11.1. Different saturated salt solutions were employed to establish different humidity conditions inside the glass tube, while the temperature remained constant at 23 °C. Initially the samples were in the green state. They were dried first and afterwards equilibrated at a relative humidity of 65 %. Then, by exchanging the salt solution, three steps in relative humidity were imposed:

- Step 1: $65 \rightarrow 95 \%$
- Step 2: $95 \rightarrow 35 \%$
- Step 3: $35 \rightarrow 65 \%$

For each step, the evolution of the moisture concentration profile with time was measured at increasingly distant time instants using MRI. The lower part of the samples was investigated, in which the major gradients could be expected (depicted as "investigated area" in Fig. 11.1), until equilibrium.

Proton nuclear magnetic resonance imaging measurements were performed at a resonance frequency of 300 MHz on a Bruker Avance II spectrometer equipped with microimaging Mic2.5 probe with a three-directional gradient of maximum 1.5 T/m. Constant time imaging sequence [21] was used with phase encoding time of 70 µm and the rf pulse length 0.5 µs. The acquired images covered a field of view of 20 mm with a spatial resolution of 78 nm. All measurements were conducted by Sergey Dvinskikh at KTH in Stockholm, Sweden, who is greatfully acknowledged again at this point for the good collaboration.

Microstructural information on the samples was gathered through SilviScan measurements [88, 62] on sample No. 1 after the MRI experiment. Since all three samples were cut from the same board, the microstructural characteristics of sample No. 2 and 3 can be assumed to be similar to that of sample No. 1. SilviScan is a measuring device developed for micro-characterization of wood, involving video-microscopy, X-ray absorption, and X-ray diffraction. It allows determination of cell dimensions in radial and tangential



Figure 11.1: Experimental setup and according model representation

material direction, wood density, and microfibril angles along thin wooden strips. Mostly radial cuts are investigated, for which the microstructural properties vary according to the growth rings (cf. density profile measurements on sample No. 1 in Fig. 11.2).

Based on this additional microstructural information the material properties \mathbf{D}_b , \mathbf{D}_v , and \mathbf{K} were determined by means of multiscale considerations as outlined in Chapters 4, 5, and 8. This allows to consider sample specific variations of these properties, resulting from the specific cell morphology determined by SilviScan. For use in the finite element model, estimates of the multiscale model for different bound water contents, temperatures, and densities, were fitted by polynomials for each material direction. For the radial direction, the homogenization step that accounts for the annual rings was omitted, since the measurements provided information on a lower scale in this direction.

The sorption behavior of the material was determined in a climate cabinet on a piece of wood from the same board as the MRI-samples. This test showed the expected behavior with a pronounced sorption hysteresis. The following set of shape parameters for Frandsen's sorption model (see Section 7.3) suitably represents the observed behavior:

$$f_1^a = 1.234, \quad f_2^a = 10.214, \quad f_3^a = -8.122, \\ f_1^d = 2.456, \quad f_2^d = 10.311, \quad f_3^d = -8.791, \\ d_1 = -1.5, \quad d_2 = 0.85.$$
(11.1)

The initial conditions at the beginning of step 1 were taken as T = 296.15 K, $\varphi_0 = 65$ % and MC = 12.1 %.



Figure 11.2: Density profile in radial direction of sample No. 1

11.3 Boundary conditions

Water transport towards the wood sample is severely limited due to the stagnant air between salt solution and wood sample, where water is transported mainly by diffusion. Such conditions can be represented by a film boundary condition for the water vapor phase. The according film boundary coefficient can be calculated as

$$k_v = \frac{D_{\rm air}(23\,^{\circ}{\rm C})}{\ell} = \frac{2.482 \times 10^{-5}\,{\rm m}^2/{\rm s}}{0.029\,{\rm m}} = 8.558 \cdot 10^{-4}\,{\rm m/s},\tag{11.2}$$

where D_{air} is the diffusion coefficient of water vapor in air [89]. ℓ denotes the distance between salt solution and wood sample (see Fig. 11.1). As for temperature, a Dirichlet boundary condition is applied on the upper side of the sample with $T = 23 \,^{\circ}\text{C}$. At the lower side of the sample, where the sample surface is exposed to air, again a film boundary condition was chosen. The film boundary coefficient is set to

$$k_T = \frac{K_{\rm air}(23\,^{\circ}{\rm C})}{\ell_1} = \frac{0.0259\,{\rm W/(m\,K)}}{0.005\,{\rm m}} = 5.180\,{\rm W/(m^2K)},\tag{11.3}$$

where K_{air} is the thermal conductivity of air. ℓ_1 was chosen as the inner radius of the NMR glass tube amounting to 5 mm.

Another process that could influence the experimental results is evaporation and condensation at the surface of the salt solution and the according changes in temperature. Due to the slow process (80 days for each step) and the distance between sample and salt solution this influence was neglected in this study. Certainly, for a smaller distance and therefore faster process the temperature change due to evaporation of water will get more and more significant and should therefore be accounted for. Alternatively, a different method to control relative humidity could (and should) be chosen, e.g. by combining the NMR measurements with a dynamic vapor sorption (DVS) device.
11.4 Comparison of experimental results and model predictions

Based on the specified sample geometry, density, material properties including sorption behavior, and boundary conditions, distributions of bound water concentration c_b , water vapor concentration c_v and temperature T were computed with the finite element model (see Figure 11.1 and Chapter 9) at the time instants as of the NMR measurements. Since the portion of water vapor is negligibly small, the macroscopic moisture concentration was calculated by multiplying the bound water concentration c_b with the local cell wall volume fraction f_{cwm} . The latter is a function of density.

In Figs. 11.3 - 11.5 the experimentally determined moisture profiles are shown together with the corresponding model results for the different steps in relative humidity. The experimental results clearly show the significant influence of the boundary conditions: Close to the surface, moisture equilibrium with the environmental humidity according to the salt solution is reached in the sample only after considerably long time, resulting in low moisture gradients inside the sample. This is most pronounced for sample No. 3 because of the relatively fast moisture transport in the longitudinal material direction, following from the longitudinally aligned hollow wood cells. As for sample No. 1, the density variations of the annual rings can be clearly seen in the moisture concentration profiles: In regions of higher density with a higher fraction of cell wall material a larger amount of bound water is found.

Comparing the model predicted moisture profiles to the corresponding experimental results shows the very good prediction quality of the numerical model. In particular, the gradients inside the investigated area are predicted very well. As for absolute values, deviations between experimental results and model predictions are obtained in the lower range of humidity. These deviations might result from the lower accuracy of the estimation of the water NMR signal intensity at lower moisture contents due to increasing relative contributions of the background signal of wood macromolecules and also from the protons in the sealing tape. Therefore the equilibrium moisture contents measured by NMR (i.e. the final moisture concentration after equilibrium) differ from that obtained within the climate cabinet (cf. Section 11.2) used for determination of the sorption behavior. Since the latter serves as input parameter in the model, the simulation approaches a different moisture content compared to the experiment. Another fact is that the NMR measurements took more than 80 days for each step, while during the experimental determination of the sorption isotherm one step lasted on average only 4 days. These different time scales could also be the reason for the deviation (see the theory proposed in Section 7.4. Besides this input value problem, the process itself is reproduced very well, which proves the suitability of the underlying physical assumptions. With one consistent set of physically meaningful parameters, the model is capable to predict transient transport processes in different material directions, for different sample densities, and different humidity steps.

11.5 Summary

In this chapter, the successful application of almost all models shown in this thesis for the simulation of moisture transport processes is presented. This is done based on a comparison of experimentally determined values with according model predictions for distributions of water concentration. Using proton magnetic resonance imaging, moisture profiles of three samples during transient change in moisture content were determined non-destructively. SilviScan measurements delivered detailed information about the morphology of the samples, serving as input for the model. The model predicted moisture profiles agreed well with the test results, underlining again the suitability of the underlying model assumptions. In addition some phenomena observed in the experiments could be explained on a physical basis, e.g. the influence of the boundary conditions on moisture distributions inside the sample. In combination with the MRI measurements, a better understanding of the underlying processes could be gained.



Figure 11.3: Comparison of experimentally determined moisture profiles (solid lines) and corresponding model results (dashed lines) for sample No. 1 (transport in radial direction) at different time instants: (a) RH step $65 \rightarrow 95 \%$, (b) RH step $95 \rightarrow 35 \%$, (c) RH step $35 \rightarrow 65 \%$



Figure 11.4: Comparison of experimentally determined moisture profiles (solid lines) and corresponding model results (dashed lines) for sample No. 2 (transport in tangential direction) at different time instants: (a) RH step $65 \rightarrow 95 \%$, (b) RH step $95 \rightarrow 35 \%$, (c) RH step $35 \rightarrow 65 \%$



Figure 11.5: Comparison of experimentally determined moisture profiles (solid lines) and corresponding model results (dashed lines) for sample No. 3 (transport in longitudinal direction) at different time instants: (a) RH step $65 \rightarrow 95 \%$, (b) RH step $95 \rightarrow 35 \%$, (c) RH step $35 \rightarrow 65 \%$

Chapter 12

Conclusions and perspectives

This thesis aims at giving a physically correct description of the hygromechanical behavior of the material wood, with a particular focus on moisture transport. To achieve this objective, several ideas and methods have been developed and applied. Starting point of all considerations is the microstructure of wood – on the microscale the behavior of wood like the viscoelastic deformation of the material or the interaction between wood and moisture can be suitably explained at least in a qualitative manner. In addition some basic constituents of wood inherent to all wood species can be defined on this small length scale. Macroscopic differences between individual wood samples therefore stem from their different chemical composition and their inherent microstructure.

Based on this physical background, a set of thermodynamically correct macroscopic balance equations is derived, forming the starting point of any hygro-mechanical analysis. Information about the material behavior enters through constitutive relations and according (macroscopic) material properties. For wood, the latter exhibit a wide variability, complicating a purely macroscopic material description. However, in the framework of continuum micromechanics it is possible to relate the macroscopic material properties to smaller length scales. Starting with material properties of the basic constituents of wood and revisiting, in a mathematical way, the influence of individual chemical composition and structure on several length scales allows to estimate the macroscopic properties of an individual sample. This is successfully done for transport properties and for viscoelastic behavior of wood under constant climatic conditions.

Particular attention is payed to sorption, which is the exchange process between water vapor in air and bound water in the wood cell walls. A purely macroscopic description of this process is hard to derive or even impossible, but looking at the smaller length scales again allows to derive a suitable description. This description is complicated by sorption hysteresis – the equilibrium moisture content at a specific relative humidity is history-dependent. To account for this phenomenon, a convenient empirical description is recapitulated first, followed by a possible theoretical description.

Finally, transient moisture transport is investigated in detail. The according mathe-

matical description involves three strongly coupled non-linear differential equations. An analytical solution of such problems at structural scale is impossible. Therefore a numerical solution is derived using the finite element method. Having this tool at hand, suitable predictions can be made for transport problems in engineering applications.

The strength of all models presented in this thesis lies in the involvement of solely input values with a clear physical meaning, circumventing the need to back-calculate model parameters from macroscopic (sample-specific) test results (except for the model for viscoelastic properties). The success of this approach is proven by several comparisons between model predictions and corresponding experimental results, justifying a more extensive model formulation compared to existing approaches in this field. It allows to explain some phenomena observed in experiments on a physical basis. This shows that a close cooperation of experimental and computational material science is very important, though not yet fully established in practice: Still computational models neglecting experimental results and experimentalists using obsolete mathematical models are encountered. As shown in this work the two disciplines may learn a lot of each other: On the one hand models without experimental validation are more or less worthless, on the other hand knowledge about the physical background and the governing equations assists the design of experiments. For example the correct consideration of boundary conditions upon the interpretation of results can be of great importance as shown in this thesis.

There are certainly several aspects in this thesis which could be further elaborated. For example, a promising idea would be to further investigate thermodynamic relationships between different material properties. After deriving the Helmholtz free energy, the thereon deduced Maxwell relations may bring out some of these connections. Another important topic is the interaction of water and wood polymers at the molecular scale. Especially regarding the rheological behavior of the wood polymers the presented model shows room for improvement. In addition a better qualitative and quantitative knowledge of the molecular processes could help to explain phenomena like mechanosorption.

As for the macroscopic continuum description, an extension of the existing finite element model for the mechanical problem would be interesting. For example this would enable a detailed investigation of the influence of climatic conditions on constructional elements. At the moment only a sequentially coupled analysis of the transport problem and the according mechanical problem is possible.

Finally, science is most fruitful when its findings are used in practice. Although the work presented in this thesis is clearly assigned to the field of basic research, the gained results help to understand the macroscopically observed behavior, which is of course also relevant in praxis. Relying upon the progress in computer technology, a comprehensive material model implemented into commercial statics software with high user-friendliness could be possible soon, enabling structural engineers to investigate critical moisture-related problems in wood constructions without the current uncertainty regarding material description and according parameters.

Overall, this work constitutes part of the required scientific basis in wood science and timber engineering that will enable – as mentioned in the beginning of this thesis – a more reliable, efficient, and intelligent use of this fascinating material.

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Publications

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Prediction of transport properties of wood below the fiber saturation point – A multiscale homogenization approach and its experimental validation. Part I: Thermal conductivity. Composites Science and Technology 71 (2011) 134–144

Eitelberger J., Hofstetter K.

Prediction of transport properties of wood below the fiber saturation point – A multiscale homogenization approach and its experimental validation. Part II: Steady state moisture diffusion coefficient. Composites Science and Technology 71 (2011) 145–151

Eitelberger J., Hofstetter K.

Multiscale homogenization of wood transport properties: Diffusion coefficients for steady-state moisture transport. Wood Material Science and Engineering 5 (2010) 97–103

Eitelberger J., Svensson S., Hofstetter K.

Theory of transport processes in wood below the fiber saturation point. Physical background on the microscale and its macroscopic description. Holzforschung 65 (2011) 337–342

Eitelberger J., Hofstetter K., Dvinskikh S.

A multi-scale approach for simulation of transient moisture transport processes in wood below the fiber saturation point. Composites Science and Technology 71 (2011) 1727–1738

Eitelberger J., Svensson S.

The sorption behavior of wood studied by means of an improved cup method. Transport in Porous Media – revision submitted for publication

Eitelberger J., Hofstetter K.

A comprehensive model for transient moisture transport in wood below the fiber saturation point: Physical background, implementation and experimental validation. International Journal of Thermal Sciences 50 (2011) 1861–1866

Eitelberger J., Bader T. K., Hofstetter K., Jäger A.

 $\label{eq:multiscale} Multiscale\ prediction\ of\ viscoelastic\ properties\ of\ softwood\ under\ constant\ climatic\ conditions.$

Computational Materials Science – submitted for publication

Additional publications and conference presentations

Additional publications

Eitelberger, J., Hofstetter, K.:

Modeling of transient moisture diffusion in wood below the fiber saturation point, Defect and Diffusion Forum 312–315 (2011) 455–459.

Conference presentations

Eitelberger, J., Hofstetter, K.:

Multiscale Homogenization of Wood Transport Properties, 3rd GACM Colloquium on Computational Mechanics, Hannover, Germany, 21/09/2009–22/09/2009 (conference paper, oral presentation).

Eitelberger, J., Hofstetter, K.:

Modeling of Moisture Transport in Wood Below the Fiber Saturation Point, 11th International IUFRO Wood Drying Conference (WDC2010), Skellefteå, Sweden, 18/01/2010–22/01/2010 (conference paper, oral presentation).

Eitelberger, J., Hofstetter, K.:

An Advanced Multiscale Approach to Stationary and Transient Moisture Transport in Wood Below the Fiber Saturation Point,

IV. European Conference on Computational Mechanics (ECCM 2010), Paris, France, 16/05/2010-21/05/2010 (conference paper).

Eitelberger, J., Hofstetter, K.:

Modeling of Transient Moisture Diffusion in Wood Below the Fiber Saturation Point, 6th International Conference on Diffusion in Solids and Liquids (DSL 2010), Paris, France, 05/07/2010–07/07/2010 (conference paper, oral presentation).

Eitelberger, J., Hofstetter, K.:

The Physical Background of Moisture Transport in Wood below the Fiber Saturation Point and its Macroscopic Description,

COST Action FP 0802 - Wood Structure/Function-Relationships, Hamburg, Germany, 05/10/2010-08/10/2010 (conference paper, oral presentation).

Eitelberger, J., Dvinskikh, S. V., Hofstetter, K.:

Combined Experimental and Numerical Investigation of Water Transport in Wood Below the Fiber Saturation Point,

COST Action FP0802 - Experimental and Computational Characterization Techniques in Wood Mechanics, Vila Real, Portugal, 27/04/2011–28/04/2011 (conference paper, oral presentation).

Eitelberger, J., Hofstetter, K.:

Derivation, implementation, and validation of a model for transient moisture transport in wood below the fiber saturation point,

7th International Conference on Computational Heat and Mass Transfer (ICCHMT 2011), Istanbul, Turkey, 18/07/2011-22/07/2010 (conference paper, oral presentation).

Curriculum Vitae

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Education

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Work Experience

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Awards	
2010	Young Scientists Award of 6th International Conference on Diffusion in Solids and Liquids 2010, Paris, France
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2002	3rd place, planning competition "Planen und Bauen", Upper Austrian state guild for building
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