Moisture-induced deformations of wood and shape memory

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Abstract. Wood is known to swell substantially during moisture adsorption and shrink during desorption. These deformations may lead to wood damage in the form of cracking and disjoining of wooden components in e.g. floor or windows. Two swelling mechanisms may be distinguished: reversible swelling/shrinkage and moisture-induced shape memory effect. In the latter, wood is deformed in the wet state and afterward dried under maintained deformation, in order that wood retains its deformed shape even after the removal of the mechanical loading, called fixation. When wood is wetted again, it loses its fixation, partially regains its original shape, called recovery. These two mechanisms have their origin at the nanoscale and are modelled here using atomistic simulation and after upscaled to continuum level allowing finite element modelling. Hysteretic sorption and swelling are explained at nanoscale by the opening and closing of sorption sites in ad- and desorption, where in desorption water molecules preferentially remained bonded at sorption sites. The moisture-induced shape memory is explained by the moisture-induced activation of the interfaces between the reinforcing crystalline cellulose fibres and its matrix at nanoscale, referred to a molecular switch. Our work aims to highlight that the understanding of sorption-induced reversible deformation and moisture-induced shape memory may play an important role in wood engineering and in building physics applications.

1. Introduction
Wood is a multiscale polymeric material, and its hygro-mechanical behaviour is highly dependent on its multiscale structure. Wood shows a cellular structure at mesoscale built of longitudinal tracheid cells containing a pore space (lumen) and a multilayer cell wall consisting of a primary (P) and three secondary layers (S1, S2 and S3) (see Figure 1a). The hygro-mechanical behavior of wood is highly determined by its thick S2 layer. The S2 layer behaves like a composite of crystalline cellulose (CC) micro-fibrils reinforcing a matrix of hemicellulose and lignin, explaining wood high stiffness and strength in the longitudinal direction. The CC micro-fibrils may show different interface configurations (Figure 1 b-c): (1) a CC-matrix parallel interface; (2) a CC-CC and CC-matrix parallel interface and (3) an undulating CC-matrix interface with CC-CC hotspots (3). These hotspots have been documented in plant cell walls [1–4]. In this study, we will reveal their important roles in the moisture-induced shape memory of wood.

The matrix is a strongly hygroscopic nanoporous material, adsorbing abundant water molecules with increasing relative humidity (RH). During sorption, the material deforms, referred to as swelling creating extra pore space. The ad- and desorption loop shows hysteresis with a higher moisture content during desorption compared to adsorption. The swelling curve also shows hysteresis, but this hysteresis
disappears when swelling is plotted versus moisture content [20]. These deformations may lead to damage in wood in the form of cracking and disjoining of wooden components in e.g. floor or windows. This swelling and shrinkage of wood is reversible and can also be used as a natural actuation mechanism, which is at the origin of the design of new functional materials with moisture-induced stimuli responsiveness, a rapidly developing field in materials science.

Figure 1. a) Secondary layers S1, S2 and S3 in wood cell wall with black lines representing the CC micro-fibrils at a small micro-fibril angle (MFA). b) Different configurations of CC micro-fibrils in the multi-component matrix. c) 1: CC-GGM parallel interface; 2: CC-CC and CC-GCM parallel interfaces; 3: undulating CC-GGM interface with CC-CC hotspots (GGM= hemicellulose galactoglucomannan). Images from [5].

Besides reversible deformation, wood shows mechanical weakening with increasing moisture content and a moisture-induced shape memory [6]–[8]. In the latter, wood is mechanically deformed in the wet state and afterward dried under maintained mechanical load, in order that wood retains its deformed shape after the removal of the mechanical loading, called fixation. When wood is wetted again, it can partially regain its original shape, called recovery. Wood fixation is used for example in furniture design to obtain permanent curved shapes. Densified wood is an example of wood fixation and an undesired effect of this type of wood is its spring back (recovery) upon being exposed again to higher moisture contents.

In this paper, we present a multiscale approach to model moisture-induced deformation and shape memory. The paper starts with a short description of the multiscale model used based on molecular dynamics (MD) and finite element modelling (FEM). In part 3, hysteretic sorption and swelling behavior of amorphous cellulose is documented and explained using MD. In part 4, we describe the moisture-induced shape memory effect and we finish with implications for practice and conclusions.

2. Multiscale modelling approach

For simplicity, the S2 layer of wood is modelled in this study as a composite of CC micro-fibrils embedded in a matrix made of the hemicellulose GGM (galactoglucomannan). In wood, the S2 composite may show three different CC-matrix interface combinations (as schematized in Figure 1 c) and we use these combinations for our CC-GGM systems. In model 1 the CC fibers are parallel to each other and embedded in a GGM matrix and only CC-GGM interfaces are present. In model 2, the CC fibers are also parallel to each other, but contacting each other thus showing both CC-CC and CC-GGM interfaces. In model 3, the CC micro-fibrils form an undulating mesh with CC-CC hotspots, while the other interfaces are CC-GGM interfaces. These representative composite units are assembled forming beams as shown in Figure 2a, which are loaded at the right top imposing a downwards displacement, while the left-hand side is considered as a symmetry axis of the beam (Figure 2 b). MD (molecular dynamics) is used to determine the moisture-dependent mechanical properties of GGM (mechanical weakening and swelling) and the interface behavior of CC-CC and CC-GGM. In this paper, we do not
provide a detailed description of the molecular dynamics methods used and the reader is referred to our publications [5], [9]–[12]. The MD study based on atomistic pull-out tests [10], [13] reveals that both the CC-CC and CC-GGM interfaces are moisture sensitive and the water molecules adsorbed in between the materials lower the maximum interface shear stress, displaying a behaviour akin to lubrication. This means that, in wet conditions, the interfaces are unlocked and can slide very easily with respect to each other, while they are mainly fixed/locked in dry conditions. The moisture-dependent interface laws are implemented using contact elements in FEM. The finite-element software used is Ansys mechanical APDL 16.2, the bulk material is modeled using PLANE182 elements and the contact elements are TARGE169 and CONTA171.

Figure 2. a) Beams of S2 layer with different CC-GGM configurations as defined in Figure 1 b) loading and boundary conditions. The half beam is loaded at the right top with a constant downward displacement d, while the left-hand side is considered as the symmetry axis of the beam. Images from [5].

3. Sorption and swelling hysteresis
The sorption and swelling hysteresis is studied using a hybrid GCMC/MD method (GCMC-Grand Canonical Monte Carlo) for amorphous cellulose. For details on the hybrid method model, we refer to [14], [15].

Figure 3 shows the hysteresis loop for (a) the sorption isotherm (moisture content versus RH), (b) swelling isotherm (strain versus RH) and (c) strain versus moisture content. The good agreement of simulated and measured sorption data shows the validity of the used atomistic model (Figure 3 a). The sorption and swelling curves versus RH show hysteresis loops, while the swelling strain versus moisture content curves in ad- and desorption collapse. This collapse of the curves means that swelling is uniquely related to the volume of water molecules adsorbed in the polymer system creating additional porosity (remark the slope of almost 1 for volumetric strain versus moisture content).

Atomistic simulations also provide information on hydrogen bonds between the polymers HB\textsuperscript{CC} (C standing for cellulose) and between polymers and water molecules HB\textsuperscript{CW} (W standing for water). The numbers of HB\textsuperscript{CC} and HB\textsuperscript{CW} are normalized to the number of glucopyranose (the monomer of cellulose) rings (for definition of hydrogen bond we refer to [14]). During adsorption, the decrease of number of HB\textsuperscript{CW} with increasing moisture content indicates breakage of the initial cellulose intermolecular bonds due to swelling of the material. The new free sorption sites on the polymetric chains created by breakage of HB\textsuperscript{CC} are then occupied by water molecules as indicated by the increase in cellulose water HB\textsuperscript{CW}. In desorption, the number of water molecules attached to cellulose indicated by HB\textsuperscript{CW} remains larger than
in adsorption, while the number of HB$^{CC}$ is smaller in desorption than in adsorption. In desorption, a hydrogen bond HB$^{CW}$ is found to be stronger than HB$^{CC}$, which means that the removal of water molecules attached to cellulose chains is not likely to occur. This means that sorption sites that became free during adsorption, remain filled by water molecules during desorption and a HB$^{CC}$ cannot reform.

This hydrogen bond analysis indicates that sorption and swelling hysteresis in wood is due to the intensive coupling of sorption and deformation (swelling/shrinkage). Swelling and breakage of polymeric hydrogen bonds lead to increased sorption of the material and, in desorption, lead to hysteresis. When swelling of the material is completely restrained, it is found that the moisture content is much lower than in normal adsorption, also known as the mechano-sorptive effect indicating an effect of stress on sorption as also found in [16] using a poromechanical approach for wood.

![Figure 3](image)

**Figure 3.** Hysteresis results. Open and closed symbols are adsorption and desorption data, respectively. a) Moisture content (m in kg/kg) versus relative humidity (RH) at T = 300K. Red circles are the atomistic results, while the blue circles are the sorption experimental data from [17]. b) Volumetric strain versus RH. c) Volumetric strain versus moisture content. d) Number of hydrogen bonds per glucopyranose ring as function of moisture content formed between cellulose HB$^{CC}$ (green circles) and between cellulose and water (red symbols). Figures from [18].

4. Moisture induced shape memory effect

The three beam models shown in Figure 2 are subjected to a particular loading protocol. First, the beam is uniformly wetted, introducing swelling in the GGM matrix. At the same time, the interfaces are wetted, weakened and mobilized, allowing slip to occur between them when loaded. We refer to this situation as that the molecular switch is on, indicating fewer hydrogen bonds exist in the interface and
slip is allowed (unlocked). The beam is then mechanically loaded at its top end, reaching a deflection $d$, where the different material components slide with respect to each other at the interfaces forming a new material configuration.

The material is then dried while keeping the load in place. The dry material interfaces again regain their strength and stiffness preventing now further slip from occurring. The molecular switch is off, locking the material configuration. We define the deflection ratio $\gamma$ as the ratio of end vertical displacement $u_y$ to length $l$. The deflection ratio in the dry loaded state $S$ is denoted by $|\gamma_S|$. Then the mechanical load is removed and the beam relaxes due to the present elastic energy, however keeping some deflection due to the locking of the interfaces preventing slipping, called fixation state. The deflection ratio in this fixation state is denoted by $|\gamma_{N'}|$. When the material is wetted again, the interfaces are weakened again and mobilized, allowing slip and losing the ability to keep the deformed shape leading to recovery towards the original shape. However, part of the deformation may remain and the initial non-deformed condition is not totally regained. Then the material is dried and some permanent deformation remains compared with the initial state. The final deflection ratio is denoted by ratio $|\gamma_{N''}|$.

Figure 4 gives the maximal deflection ratio at the end of the beam for the dry loaded stage $S$, for the unloaded dry state $N'$ (fixation state) and for the final dry state after rewetting and drying $N''$ (recovery state). Remark the logarithmic scale of the y-axis. The deflection ratio for the three models in dry loaded state $S$ is almost the same since the deflection is mainly controlled by the imposed mechanical load.

In the fixation state $N'$, the deflection ratio is highest for model 3 and lowest for models 1 and 2. For the laminated models 1 and 2, showing parallel CC layers, less sliding occurs in the interfaces during loading and as such more spring back will occur upon mechanical unloading, leading to lower fixation and deflection ratio. In contrast, for model 3, the undulating reinforcing structure showing a rather high bending stiffness, leads to higher shear stresses in the interfaces and more sliding in the interfaces. When unloading, the interfaces and especially the CC-CC hot spots prevent spring back and contribute to the locking and fixation of the deformed shape.

All the systems show a deflection ratio $N''$ at recovery close to the ratio at fixation, showing that subsequent wetting and drying does not affect the fixation state and deformations remain locked.

In addition, a model was investigated where the weakening of the interfaces in model 3 was turned off. For this model no fixation was possible, meaning the system regained its initial shape after removal of external displacement, showing no moisture-induced shape memory effect. This shows that interface weakening and strengthening upon wetting and drying, the so-called molecular switch, is at the origin of the moisture-induced shape memory effect.

![Figure 4](image_url)

**Figure 4.** Deflection ratio at the right edge for the models 1, 2 and 3 for states $S$, $N'$ and $N''$. Figure from [5].
5. Practical consequences and conclusions
In this paper, we showed that atomistic modelling and finite element upscaling can be used as a multiscale method to study the hygro-mechanical behaviour of wood.

Atomistic modelling of amorphous cellulose shows that sorption and swelling hysteresis are found to be reversible and can be explained by the coupling between swelling and sorption. During adsorption, new sorption sites are made available by the breakage of polymer hydrogen bonds due to swelling. These new sites are then occupied with water molecules showing strong polymer-water hydrogen bonds. In desorption, these strong hydrogen bonds remain and prevent the removal of water molecules leading to higher moisture contents and strains in desorption than adsorption. This finding is important with respect to the behaviour of wood exposed to cyclic moisture loading, as happens to wood in outside and inside environments. Based on our results, we can conclude that wood, when exposed to small RH cycles, like for instance occurs for wooden artifacts in controlled environments as in museums, will only show small intermediate scanning loops in moisture content and as consequence small changes in swelling. These small moisture-induced deformations due to hysteresis prevent moisture-induced mechanical damage to wood such as cracking. Further, based on our findings, we can conclude that we can further reduce changes in swelling and hysteresis by making wood stiffer (e.g. densified or compressed wood) or by reducing its hygroscopicity (by reducing its moisture-solid interactions by removing sorption sites by chemical treatment).

We showed that moisture-induced shape memory is due to a molecular switch weakening the crystalline cellulose micro-fibril interfaces when loaded in wet conditions, allowing important wood deformation, resulting in a fixation of the shape after drying again and removing the mechanical loading. Moisture-induced shape memory is more and more used in the treatment of wood to achieve high-density wood with high stiffness used in wooden furniture and modified wood for construction. This highly densified wood can however show stringback during repetitive wetting/drying recovering, at least in part, its original properties and shape. Spring back can be prevented when no moisture weakening occurs in interfaces and water does not work as a molecular switch. These new insights can lead to new treatments of wood to improve its moisture related properties.

In this paper, we studied the shape memory effect in wood cell walls at the nanoscale. We remark that the finite element modelling was limited to 2D simulations, and should be extended to 3D in future research. It was also shown in [19] on studying the moisture behaviour of a cut half-cell, that moisture-induced shape memory of wood may be influenced by the cellular arrangement, which is beyond the scope of the present study. The shape memory effect of wood may find its origin at multiple scales, which should be the topic of future research.

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