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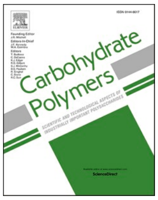

Review

# Combining scattering analysis and atomistic simulation of wood-water interactions

Paavo A. Penttilä [a,*], Antti Paajanen [b], Jukka A. Ketoja [b]

[a] Department of Bioproducts and Biosystems, Aalto University, P.O. Box 16300, FI-00076 Aalto, Finland
[b] VTT Technical Research Centre of Finland Ltd, P.O. Box 1000, FI-02044 VTT, Finland

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## ABSTRACT

Molecular-scale interactions between water and cellulose microfibril bundles in plant cell walls are not fully understood, despite their crucial role for many applications of plant biomass. Recent advances in X-ray and neutron scattering analysis allow more accurate interpretation of experimental data from wood cell walls. At the same time, microfibril bundles including hemicelluloses and water can be modelled at atomistic resolution. Computing scattering patterns from atomistic models enables a new, complementary approach to decipher some of the most fundamental questions at this level of the hierarchical cell wall structure. This article introduces studies related to moisture behavior of wood with small/wide-angle X-ray/neutron scattering and atomistic simulations, recent attempts to combine these two approaches, and perspectives and open questions for future research using this powerful combination. Finally, we discuss the opportunities of the combined method in relation to applications of lignocellulosic materials.

## 1. Introduction

Moisture content and its changes influence the processability and usage of cellulosic biomass on multiple levels of its hierarchical structure. The interactions between water and wood cell wall nanostructure govern the mechanical properties of wood as a material (Kretschmann, 2010) and determine its vulnerability to biological degradation (Brischke & Alfredsen, 2020). The delicate interplay between water and the nanoscale building blocks of the plant cell wall is especially crucial for applications utilizing self-assembly of nanocelluloses (Kontturi et al., 2018).

Despite their extreme importance and a long history of research (Engelund, Thygesen, Svensson, & Hill, 2013), wood-water interactions are still far from being fully understood. This has been at least partly a methodological challenge, because very few tools are available for nanoscale structural characterization of wood and wood-based materials under various moisture contents (Plaza, 2019). X-ray and neutron scattering techniques hold a promise for this purpose, as they can be used to efficiently determine the average nanoscale structure in a macroscopic sample volume and, even more importantly, under various external conditions and with hardly any sample preparation (Martínez-Sanz, Gidley, & Gilbert, 2015; Rongpipi, Ye, Gomez, & Gomez, 2019). However, the interpretation of scattering data especially in the small-angle regime is not straightforward, and the data analysis often requires support from other, complementary techniques.

Computation or simulation of scattering intensities based on locations of atoms as determined by atomistic simulations can be used to directly link the evolution of a real-space structure to scattering data. Computed scattering data can be directly compared to its experimental equivalent and used to elucidate the origin of features and changes observed in the data. At the same time, it helps in finding ways to improve both the atomistic models and the models used to analyze scattering data. Despite being commonly applied in other fields, such as for determining protein structures (Srivastava, Tiwari, Miyashita, & Tama, 2020), this route is still rather unexplored for hierarchical cellulosic materials and their interaction with moisture.

In this perspective article, we introduce the basic features of the methods and offer a brief summary of previous research dealing with computed scattering patterns for cellulosic materials. Finally, we explore the possibilities of merging atomistic simulations with X-ray and neutron scattering analysis. We focus particularly on aspects related to the fundamentally important but complex interactions between water and the nanostructure of wood cell walls.

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* Corresponding author.
*E-mail address:* paavo.penttila@aalto.fi (P.A. Penttilä).

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## 2. Scattering methods for studying moisture effects

Elastic scattering of X-rays and neutrons provide non-destructive techniques for analyzing the structure of materials from the atomic level to several hundreds of nanometers. X-ray scattering is based on the interaction of X-rays with the electron cloud of the sample's atoms, whereas neutrons interact primarily with the nuclei and are sensitive to different isotopes. X-rays for scattering experiments are produced either with laboratory sources or by synchrotrons, whereas neutrons are available at large-scale facilities only. Scattering methods have become indispensable tools for elucidating the structure of cellulosic materials and the effects of various processes on it.

Wide-angle X-ray scattering (WAXS), including X-ray diffraction, is sensitive to the molecular scale organization of materials ($10^{-10}$–$10^{-9}$ m) and, in particular, the crystalline portion of cellulose microfibrils (thickness 2–3 nm in wood). It is widely applied to analyze microfibril orientation, cellulose crystallite size and sample crystallinity in various types of cellulosic materials from wood to pulps and nanocelluloses. The crystal size (the coherence length of atomic-level crystalline order) and lattice spacings (distances between molecular sheets in the crystal) can be determined in different directions relative to the crystal orientation. In experimental WAXS data (Fig. 1a, c), water produces a wide, isotropic contribution, which can be subtracted (Leppänen et al., 2011; Thomas et al., 2013) in order to reveal any differences in the remaining scattering intensity. The neutron equivalent of WAXS, wide-angle neutron scattering (WANS), is less commonly utilized, but has proven useful for detecting diffraction contributions from different crystalline cellulose fractions depending on their accessibility to water (Thomas et al., 2013, 2014, 2015).

WAXS studies of cellulosic materials undergoing moisture changes (as summarized, *e.g.*, by Agarwal, Ralph, Baez, Reiner, and Verrill (2017)) have exposed some fundamental questions related to the molecular-scale interactions between the cellulose crystallites and water. For instance, several studies on materials ranging from bacterial cellulose and cotton (Fang & Catchmark, 2014) to native woods (Penttilä et al., 2020) have reported an increase in the 200-peak width (typically by 5%–20%) due to removal of water (Fig. 1c). Based on the Scherrer equation (Cullity & Stock, 2001), this can be interpreted as a decrease of the coherence length of crystalline order or "crystal size" with moisture content. At the same time, the positions of the diffraction peaks shift, indicating a larger (200) lattice spacing (typically by 1% or below) and thus looser packing of the cellulose chains in the microfibrils after drying. Reasons such as interactions with a shrinking polymer matrix (Abe & Yamamoto, 2005; Yamamoto et al., 2010), formation of intrachain hydrogen bonds (Hill et al., 2010), and stresses due to water condensation (Zabler, Paris, Burgert, & Fratzl, 2010) have been proposed to explain these observations. Nevertheless, their exact molecular-scale mechanism remains to be confirmed.

Scattering close to the direct path of the X-ray beam, termed small-angle X-ray scattering (SAXS), arises from nanometer-sized domains ($10^{-9}$–$10^{-7}$ m) with different electron density from their surroundings (Porod, 1982). In the case of a water-saturated plant cell wall, SAXS exhibits a contribution from the crystalline cellulose microfibrils in a continuous matrix of water, less-ordered polysaccharides, and lignin. Drying of the sample changes the contrast conditions, and scattering from surfaces of air-filled pores starts to dominate the pattern especially at lower scattering angles (Fig. 1d). In the case of small-angle neutron scattering (SANS), the neutron version of SAXS, the scattering length density landscape looks different, making SANS sensitive to slightly different structures in a multicomponent system than SAXS. Perhaps most importantly, the sensitivity of SANS is different to hydrogenated and deuterated water ($H_2O$ and $D_2O$), enabling the technique of contrast variation (Heller, 2010). This property is most commonly utilized when increasing the scattering contrast between cellulose microfibrils and water by replacing $H_2O$ with $D_2O$ (Martínez-Sanz et al., 2015). SANS and SAXS can also be applied simultaneously to the same sample volume (Metwalli et al., 2020), which yields complementary information especially useful for the analysis of complex systems.

SAXS and SANS studies in the past have given consistent results for the nanoscale behavior of cellulosic materials with moisture changes. In particular, several studies have shown a correlation between the moisture content and center-to-center distance between individual microfibrils (from around 3 nm in dry state to 3–4 nm or above in wet state) in the cell walls of wood (Fernandes et al., 2011; Jakob, Tschegg, & Fratzl,

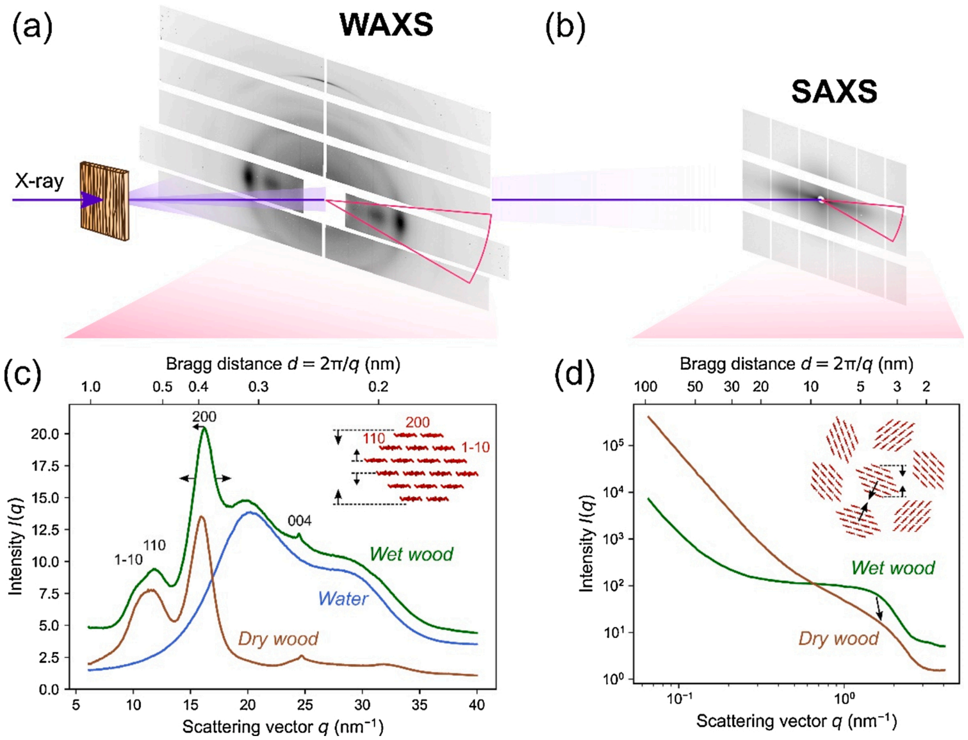

**Fig. 1.** Examples of X-ray scattering data from spruce wood (data from Penttilä et al. (2020)): two-dimensional (a) WAXS and (b) SAXS patterns from dry wood, equatorial (c) WAXS and (d) SAXS intensities from wet and dry wood plotted as a function of the magnitude of the scattering vector ($q = 4\pi \sin(\theta)/\lambda$, where $\theta$ is half the scattering angle and $\lambda$ wavelength). The one-dimensional intensities in (c) and (d) have been obtained by azimuthal integration over the sectors indicated in the two-dimensional patterns (a) and (b). Arbitrarily scaled WAXS intensity of pure water is included in (c). The size scale of structures scattering at $q$ can be roughly estimated by the Bragg distance $d = 2\pi/q$ (secondary horizontal axis in (c) and (d)). Drying-related changes in the scattering intensities and the molecular scale structure of cellulose microfibrils and microfibril bundles (insets in (c) and (d)), as discussed in the text, are illustrated by arrows in (c) and (d).

1996; Penttilä, Rautkari, Österberg, & Schweins, 2019, 2020; Plaza, Pingali, Qian, Heller, & Jakes, 2016), bamboo (Thomas et al., 2015), and celery collenchyma (Kennedy, Šturcová, Jarvis, & Wess, 2007; Thomas et al., 2013), although the changes seem generally smaller in angiosperms than in conifers (Leppänen et al., 2011; Penttilä et al., 2019, 2020; Thomas et al., 2014; Thomas, Martel, Grillo, & Jarvis, 2020). Similar dependencies have been observed in processed celluloses such as pulps (Mao, Heck, Abushammala, Reiter, & Laborie, 2019; Testova et al., 2014), cellulose nanofibrils (Penttilä et al., 2013), and cellulose nanocrystals (Liu et al., 2018). SAXS and SANS results indicating a decreasing lateral width of the microfibrils (typically by 10%–20%) at low moisture contents have also been published at least for wood (Cheng et al., 2011; Penttilä et al., 2019, 2020; Suzuki & Kamiyama, 2004). These latter observations might be associated with the changes of WAXS peak widths, even though, again, their origin on the molecular level is not understood.

With the continuous development of more powerful sources of X-rays and neutrons, including laboratory instruments for X-rays, it has become possible to use X-ray and neutron scattering for following dynamic processes such as sorption phenomena in real time. Despite recent improvements in small-angle scattering analysis of wood and wood-based materials as a function of moisture (Barbetta, Fratzl, Zemb, & Bertinetti, 2017; Mao et al., 2019; Penttilä et al., 2019; Plaza et al., 2016), however, we are still far from a cohesive picture of the information included in scattering data from such systems. Especially, small-angle scattering models correspond only to an approximated nanoscale morphology of the sample and are unable to explain the exact molecular-scale interactions behind the observed changes with moisture. A similar challenge is faced in the analysis of WAXS data, where the underlying reasons for observed structural changes remain unclear and even their effect on the scattering data is not self-evident. Therefore, the help of other methods is required to reveal the detailed architecture of the plant cell wall and its relationship with moisture.

## 3. Atomistic simulation of microfibril bundles

Atomistic simulation methods can be used to probe molecular-level structures and processes that are difficult to observe experimentally. Among them, molecular dynamics (MD) simulation is a technique for solving the time evolution of an atomistic system from a given initial state and environmental conditions. The atoms are considered point-like particles that move according to the classical equations of motion, while the interatomic forces are described using an empirical potential energy function. The functional form of the energy expression and the associated set of parameters constitute what is called a force field—a determining factor for the quality of the model. Practical simulations can address systems with a length scale of tens of nanometers and a time scale of microseconds. Atomistic simulations are also carried out using stochastic techniques, *i.e.*, Monte Carlo (MC) methods, which in the broadest sense refer to any simulation technique based on random numbers. For instance, Metropolis MC is used to simulate thermodynamic ensembles, whereas kinetic MC is applied for thermally activated processes. In practice, MD simulations are often carried out within a wider stochastic scheme.

The availability of crystallographic information on native cellulose (Nishiyama, Sugiyama, Chanzy, & Langan, 2003; Nishiyama, Langan, & Chanzy, 2002) and force fields for carbohydrates (Foley, Tessier, & Woods, 2012) have enabled molecular simulations at the level of cellulose microfibrils and their assemblies (Fig. 2). Most of the reported modelling focuses on crystalline surfaces and individual microfibrils. While several studies address the interactions of cellulosic surfaces with water (Bergenstråhle, Wohlert, Larsson, Mazeau, & Berglund, 2008; Lindh, Bergenstråhle-Wohlert, Terenzi, Salmén, & Furó, 2016; Maurer, Sax, & Ribitsch, 2013; O'Neill et al., 2017; Petridis et al., 2014), only a few look at the role of water in the structure of microfibril bundles, a fundamental structural unit of wood cell walls (Adobes-Vidal, Frey, & Keplinger, 2020; Terrett et al., 2019).

Among the earliest reports, Langan et al. (2014) showed that high temperatures, such as those encountered during a steam explosion pre-treatment, lead to an irreversible loss of interfacial water, and, consequently, to a closer packing of the fibrils and their partial co-crystallization. Notably, their work involved the use of computed scattering patterns to support the interpretation of related X-ray fiber diffraction data. Kulasinski and co-workers studied the role of the

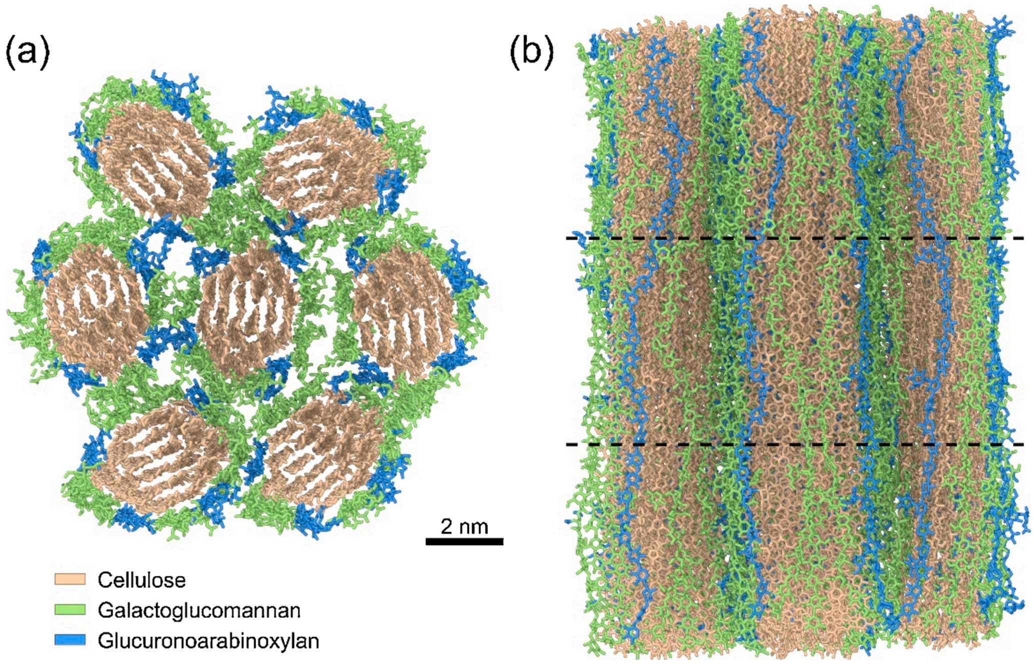

**Fig. 2.** Example of an atomistic model of a cellulose microfibril bundle: (a) along the fibril axis, (b) perpendicular to the fibril axis (section corresponding to (a) marked by dashed lines). Each of the seven fibrils consist of 18 cellulose chains, 30 glucose units long. Such models are used to represent softwood cellulose microfibril bundles in our ongoing work.

cellulose-hemicellulose interface in the moisture-induced swelling of wood (Kulasinski, Guyer, Derome, & Carmeliet, 2015), and later extended their model to address the effects of hydration on the elastic properties of the cell wall (Kulasinski, Derome, & Carmeliet, 2017). More recently, Paajanen, Ceccherini, Maloney, and Ketoja (2019) demonstrated the possibility of chirality transfer from microfibrils to their bundles, and its consequences for the bundle structure and the bound water of the cell wall. Lastly, Chen, Terenzi, Furó, Berglund, and Wohlert (2019) established molecular simulation as a means to decompose $^{13}$C NMR longitudinal relaxation time distributions into contributions from specific locations within hydrated cellulose nanofibril aggregates. Microfibril aggregation was also addressed in a number of earlier works (Oehme et al., 2015; Paajanen et al., 2016; Sáenz Ezquerro, Crespo Miñana, Izquierdo, & Laspalas, 2019; Silveira, Stoyanov, Kovalenko, & Skaf, 2016; Wei, Sinko, Keten, & Luijten, 2018), which focused on aggregation during cell wall biosynthesis or due to interfacial interactions.

Molecular dynamics can also be studied using coarse-grained models, which may help to overcome the time and length scale limitations of atomistic resolution models of the plant cell wall nanostructure. In the coarse-graining approach, the spatial resolution of the molecular model is reduced from atomistics to that of functional groups or repeating units of the polymer structure, or even larger entities. This reduces the number of degrees of freedom and makes simulations of larger systems and longer times feasible. Recently, there have been efforts to develop coarse-grained molecular models of cellulose and hemicelluloses, as summarized by Mehandzhiyski et al. (2020). From the viewpoint of plant cell wall research, such models are beneficial for two reasons. Firstly, they can be used to represent larger segments of the cell wall, and thus address structural organization beyond the level of individual microfibril bundles. Secondly, the study of dynamics can be extended beyond the microsecond range, which enables direct simulation of slow processes, such as those involved in swelling. However, atomistic scale details are not reproduced by these models.

## 4. Computed scattering patterns

X-ray and neutron scattering patterns are readily calculated from an atomistic model given the direction of the incident beam and following the elastic and single-scattering approximations. In most cases, however, it is not meaningful to compare such patterns directly against an experimental reference. This is because of the averaging nature of the scattering measurement. An experimental pattern arises due to a vast number of scattering objects in a macroscopic sample, which has at least some structural heterogeneity. An atomistic model, on the other hand, represents a unique configuration within a nanometer-scale sub-volume—both with respect to the internal arrangement of the atoms and its orientation relative to the beam. For this reason, some form of stochastic approach is required.

A common technique is to apply spherical or cylindrical averaging to the equation that relates the atomic coordinates with the scattering intensity. The assumption of spherical symmetry yields the Debye scattering equation (Gelisio & Scardi, 2016), which can be used to calculate isotropic powder patterns. These are representative of a powder-like sample with random orientation of constituent particles. Similarly, azimuthal averaging around a chosen axis yields the cylindrically symmetric form, which can be used to calculate fiber patterns. These represent a sample with parallel, often fibrillar constituent particles with random orientation around the fiber axis. The latter case is relevant for studies of wood cell wall nanostructure, which involves a preferred orientation of microfibrils. It is also possible to account for a distribution of orientations *via* further post-processing of a single fiber pattern (Nishiyama, Johnson, & French, 2012). Heterogeneity in the molecular arrangement can be taken into account by considering an ensemble of models instead of a single one. Moreover, the search for correspondence can be formulated as an optimization problem, in which experimental data is matched against a weighted average from a library of pre-computed patterns (Zhang, 2016).

In the study of cellulosic materials, computed scattering patterns have been primarily used to address the size, shape and internal structure of the microfibril (Hadden, French, & Woods, 2014; Kubicki et al., 2018; Langan et al., 2014; Lindner, Petridis, Langan, & Smith, 2015; Newman, 2008; Newman, Hill, & Harris, 2013; Nishiyama et al., 2012; Thygesen, Oddershede, Lilholt, Thomsen, & Ståhl, 2005; Yang & Kubicki, 2020; Zhang, 2016). This includes studies on specialized topics, such as effects that arise from conformational disorder of the exocyclic groups, the presence of hydration layers, and the possibility of a helical twist. More applied topics, such as the effects of dilute acid and steam-explosion pre-treatments (Inouye et al., 2014; Langan et al., 2014) on the nanostructure of biomass have also been reported. The needs of the cellulose research community have also prompted the development of algorithms for efficient calculation of fiber patterns on distributed systems (Yu et al., 2015; Zhang, Yu, Kaeli, & Makowski, 2014, 2016). It is to be noted, that most studies in the past have relied on 36-chain models for the cellulose microfibril, whereas recent evidence supports a smaller number of chains (Jarvis, 2018; Nixon et al., 2016) and the 2-3-4-4-3-2 arrangement of glucan chains in six layers for the most plausible cross-sectional shape in plant cell walls (Yang & Kubicki, 2020) (Fig. 3).

Extending the use of atomistic models and computed scattering patterns from individual microfibrils to the level of their bundles opens a number of possibilities in plant cell wall research. Especially when including also non-cellulosic cell wall components in the models, we can essentially cover the molecular architecture forming the basis of the plant cell wall (Terrett et al., 2019). This is enabled by the size of microfibril bundles that can be currently simulated in atomistic detail, *i.e.*, approximately 10–20 nm in diameter, which coincides with the size of these structures in spruce wood (Adobes-Vidal et al., 2020). Furthermore, the same length scale is covered by SAXS and SANS, which enables us to link the models with experiments by computing scattering intensities in the small-angle regime. At the same time, by including other cell wall polymers and bound water in the models of microfibril bundles, we can address their contributions to the scattering patterns. This is especially interesting for hemicelluloses, which have been shown to associate closely with the microfibrils (Jarvis, 2018). Lastly, we can use the same approach to study dynamic processes that alter the nanometer scale structure of the cell wall. This can be done, for example, by using a sequence of models to represent a hypothetical structural transition. The moisture-induced swelling of wood is an example of a natural process of particular interest.

## 5. Towards a combined analysis

Combining X-ray and neutron scattering experiments with atomistic simulations *via* computed scattering patterns has a high potential for new discoveries. Besides helping the development of both types of tools individually, this approach is likely to yield completely new results on the structure of cellulosic materials and their interaction with moisture. Such breakthroughs have recently become possible, on one hand, due to the developments in the modelling capabilities and scattering data analysis and, on the other hand, due to the more accurate picture of cellulose microfibril bundles that can serve as the basis of model-building for both methods. Therefore, we as a collaborative effort between Aalto University and VTT are currently exploring a combinatory approach by:

1. Computing SAXS and WAXS intensities based on atomistic simulations of cellulose microfibril bundles, including hemicelluloses and water
2. Comparing the atomistic models and computed scattering intensities to experimental data and using the information to improve the models

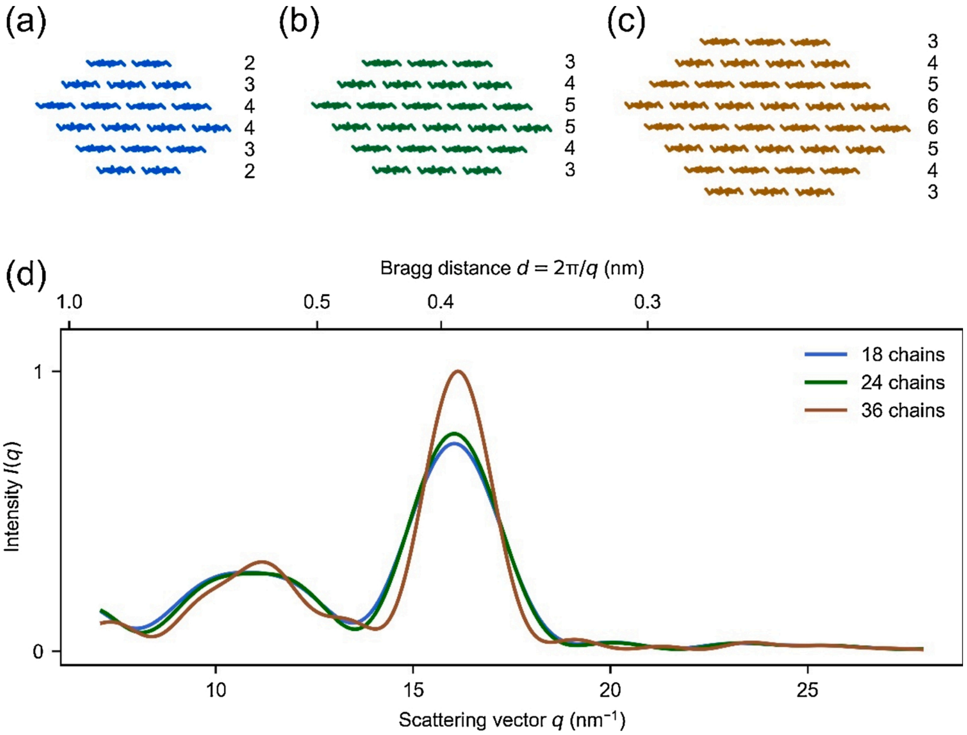

**Fig. 3.** Equatorial WAXS intensities calculated from three atomistic models of a cellulose microfibril: (a) 18-chain fibril in a 2-3-4-4-3-2 stacking, (b) 24-chain fibril in a 3-4-5-5-4-3 stacking, (c) 36-chain fibril in a 3-4-5-6-6-5-4-3 stacking. The scattering calculations shown in (d) are part of our ongoing work, following those of Kubicki et al. (2018) and Zhang (2016).

3 Addressing the molecular scale mechanisms of moisture-induced swelling of microfibril bundles

Our combinatory approach essentially builds the gap between the detailed molecular-scale structure, as obtained from the simulations, and the averaged scattering data on molecular assemblies and larger structural components of the plant cell wall. Instead of having to rely on approximate models and assumptions, the features observed in experimental data can be linked to real-space structures, and their changes can be studied systematically. This will allow developing the models used for scattering data analysis as well as fresh insights into previously reported anomalies and open questions: (*i*) effects of microfibril aggregation and a dynamic water-hemicellulose layer between them on scattering data, (*ii*) relationship between cellulose microfibril dimensions and the corresponding quantities determined from scattering data, (*iii*) different causes of deviations from the "ideal" cellulose crystal structure (small crystals, localized disorder, thermal motion, twisting, curving) and their contribution to WAXS data, and (*iv*) contributions of twisting and curving of individual and bundled microfibrils as well as occasional joins between neighboring fibrils to small-angle scattering data. At the same time, constant comparison with experimental data provides opportunities for building and validating the models for simulations.

The ability to simulate aggregates or bundles of cellulose microfibrils, with accurate dimensions and together with hemicelluloses and water, opens a route to more complete description of some of the most important properties of plant cell walls and plant-based materials. By combining the new modelling capabilities with the benefits of X-ray and neutron scattering methods, including possibilities for *in situ* characterization and well-representative nature of data, more light on phenomena such as the molecular-scale interactions between wood nanostructure and water can be gained.

## 6. Combined approach enables exploiting moisture

Lignocellulosic polymers have already proven to be a valuable basis for several large-scale industries, where their unique polymer-water interaction is both an asset and a challenge. Moisture changes have been used in conventional construction materials and paperboard industry to form strong bonds between different structural components, which allows various bio-based materials to be produced by sustainable processes. On the other hand, the production and application performance of lignocellulose-based materials can be highly sensitive to changes in ambient relative humidity. The rather universal exponential trends of viscoelastic and creep behavior with moisture, found in various cellulosic materials, suggest a molecular origin for the relevant mechanisms (Ketoja, 2008; Kulasinski, Guyer, Keten, Derome, & Carmeliet, 2015; Nissan, 1976). The same holds for the absorption, diffusion and swelling dynamics of wood fibres that are critical in the many end uses. However, until now it has been impossible to point out precisely, which hierarchical level of a structure accounts for the observed phenomena.

Understanding and exploiting the moisture effects in cellulosic materials allows both improving the existing applications and developing new ones. The approach of combining scattering experiments with atomistic simulations helps in revealing the exact role played by each nanoscale structural feature. This enables selecting the most suitable components to optimize performance in each application or targeting chemical or enzymatic modifications to the structural features that are most relevant for a specific application or process. With the new knowledge, we expect the use of lignocellulosic polymers to expand beyond current applications and industries. This includes, for example, optimization of processes taking place in biorefineries (Kallioinen, 2014), more detailed description of cellulose dissolution processes (Medronho & Lindman, 2015), construction of nanoporous templates for photosynthetic microbial biofuel production (Jämsä et al., 2018), utilizing evaporation-induced self-assembly of cellulose nanocrystals for anisotropic adhesion (Tardy et al., 2020), and numerous other applications (Ajdary, Tardy, Mattos, Bai, & Rojas, 2020; Kontturi et al., 2018) taking advantage of the special relationship between cellulosic materials and water. Being recyclable, biocompatible, biodegradable, and safely processable, wood-based polymers meet all key environmental requirements of future materials bioeconomy, once their secrets are revealed.

## CRediT authorship contribution statement

**Paavo A. Penttilä:** Conceptualization, Writing - original draft, Writing - review & editing, Visualization, Project administration, Funding acquisition. **Antti Paajanen:** Conceptualization, Writing - original draft, Writing - review & editing, Visualization, Project administration, Funding acquisition. **Jukka A. Ketoja:** Conceptualization, Writing - original draft, Writing - review & editing, Funding acquisition.

## Declaration of Competing Interest

The authors report no declarations of interest.

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