

Water diffusion in wood and plant cell walls: An activated process

Luoyi Yan¹, Rahima Sidi-Boulénouar, Wafae Bagui², Jaime Gil-Roca³, Benjamin Maillet, Laurent Brochard⁴, and Philippe Coussot^{1*}

Laboratoire Navier (Ecole Nationale des Ponts et Chaussées, Université Gustave Eiffel, and CNRS), 77420 Champs sur Marne, France

 (Received 31 March 2025; revised 27 June 2025; accepted 15 August 2025; published 1 October 2025)

Wood, plants, and cellulosic materials contain significant amounts of bound water, up to 30% of their dry mass, present as nanoscale inclusions of water molecules within a solid matrix. This bound water is mobile and exchanges readily with vapor and free water; however, its transport dynamics remain poorly understood due to the lack of direct observations. In this study, nuclear magnetic resonance and magnetic resonance imaging were used to characterize bound water diffusion in various wood types and cellulose fibers across different directions and at different temperatures. To isolate bound water dynamics, the accessible pores were filled with oil, and bound water distribution was tracked during desorption. The results demonstrated that bound water diffusivity is independent of both its concentration and its direction, despite the pronounced anisotropy of wood, and exhibits an exponential dependence on the inverse of the temperature. These observations suggest that bound water transport is an activated process, analogous to the diffusion in solids, with an activation energy comparable to the latent heat of liquid water evaporation. These findings show that bound water enables efficient long-distance moisture transport through wood and plant structures, irrespective of whether the voids are closed, empty, or filled with nonaqueous liquid, provided a local bound water deficit exists. Consequently, bound water spontaneously refeeds a desaturated plant system. This phenomenon plays a fundamental role in water extraction, water imbibition, and moisture transport in living plants and cellulosic materials.

DOI: [10.1103/5qm8-trjr](https://doi.org/10.1103/5qm8-trjr)

I. INTRODUCTION

Wood, plants, and other cellulosic materials such as paper or natural textiles can absorb water in their pores (or voids) but also in the amorphous regions between the cellulose microfibrils [1–3]. This absorbed water, commonly referred to as “bound water” or “cell-wall water,” forms nanoscale inclusions of one or a few molecules inside the solid structure through hydrogen bonding [4] (see Fig. 1). This phenomenon drives the swelling [see Figs. 1(b) and 1(c)] or shrinkage of cellulosic materials [4–6] under differing humidity conditions, potentially leading to wood structure damage [6,7]. The bound water content in the solid phase of the material increases with ambient relative humidity, and can reach up to 30% of the dry mass of the material [8]. Although poorly characterized and understood, the absorption and transport processes of this bound water are of fundamental importance in a

myriad of applications. For example, these processes contribute to humidity regulation, enhancing indoor comfort in buildings partly or fully made of bio-based materials such as wood, insulating fiberboard (flax, cotton, hemp), hemp concrete, or raw earth walls [9–12]. In timber drying processes, the extraction of the final bound water fraction is the primary factor controlling the drying rate [13], and this is also the critical stage during which material defects such as fractures can appear [14]. Similarly, in paper production, the extraction of the final fraction of bound water represents the most-energy-intensive phase in paper mills [15], and most of the functional properties of paper are developed during this stage [16]. Moreover, in cellulosic sheets, variation in bound water content caused by storage, heating, or ink printing can lead to mechanical instabilities such as curls or cockles [17–19].

Recently, several intriguing observations suggest that despite being confined and dispersed in nanopores between solid microfibrils, bound water plays a crucial role in water transport within wood and plants. During imbibition, bound water penetrates wood structure ahead of free water [20–24], significantly slowing the capillary penetration [22–24] by several orders of magnitude in time. Furthermore, nuclear magnetic resonance (NMR) observations further reveal that during slow drying, the concentration of

*Contact author: philippe.coussot@univ-eiffel.fr

Published by the American Physical Society under the terms of the [Creative Commons Attribution 4.0 International](https://creativecommons.org/licenses/by/4.0/) license. Further distribution of this work must maintain attribution to the author(s) and the published article's title, journal citation, and DOI.

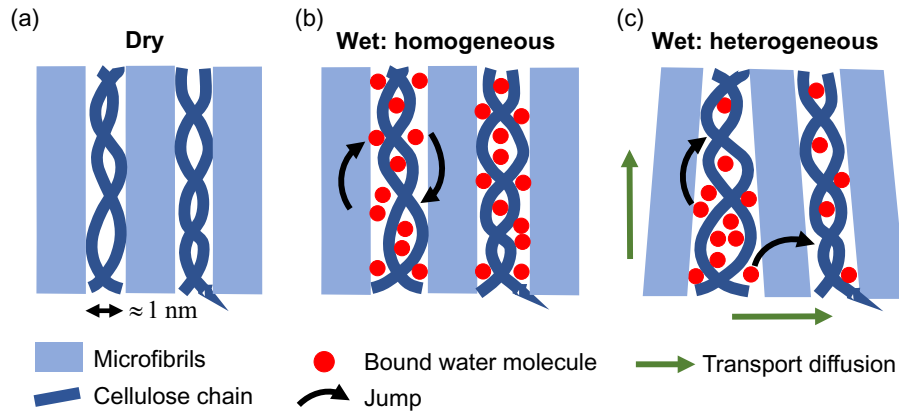


FIG. 1. Structural element of a cellulose fiber (or wood cell wall) in a cellulosic material with crystalline regions (microfibrils composed of bundled cellulose chains) separated by amorphous regions (with entangled cellulose chains or hemicellulose chains in wood). (a) Dry state. (b) Homogeneous wet state, with a uniform concentration of bound water molecules adsorbed in the amorphous regions; self-diffusion does not affect the concentration. Note the swelling of the structure. (c) Heterogeneous wet state, with a nonuniform bound water concentration leading to transport diffusion. Water moves from regions of higher to lower concentration in any direction, creating a swelling gradient and structural deformation.

bound water decreases only after most of the free water has disappeared [21,25,26]. More recent analyses suggest that bound water also ensures the extraction and transport of free water from the interior of wood to its surface during most of the drying process [27,28]. Additionally, experiments with cellulose fiber stacks immersed in oil have demonstrated that bound water transport can occur within the cellulose fiber network [29].

Therefore, gaining a more comprehensive understanding of the physical properties of bound water is critically important. Particularly, it is essential to understand its specific transport dynamics within the solid structure. This is the aim of the standard tests for measuring the (apparent) moisture diffusion through a hygroscopic material, i.e., either from the steady-state vapor flux through a material layer (wet or dry cup test [30,31]) or from the transient diffusion in a material layer [32]. Some approaches have also provided information on the bound water distribution along one direction during these tests [33] or during the final stages of wood drying [28]. However, in materials such as wood [34,35] and paper [36,37], once free water is absent, bound water diffusion within cell walls (or cellulose fiber structures) and vapor diffusion through lumens (or voids) both contribute to the overall moisture transport. As a consequence, all the above-mentioned approaches assess only global moisture transport, encompassing both diffusive transports and phase exchanges (sorption and desorption) between bound water and free water [4]. This limitation likely contributes to the widely differing diffusion coefficients (over more than 5 decades) reported in the literature for different wood types (see the data summary in Ref. [13]).

Consequently, it is essential to independently observe and fully characterize bound water transport within cell

walls. However, unlike capillary water in micron-sized channels, which can be directly imaged, visualization of the small clusters of water molecules embedded within the solid structure of cellulosic systems remains a significant challenge. Moreover, to isolate bound water transport and prevent vapor interactions, the lumens must be filled with an alternative fluid phase, which further complicates direct observation of the cell wall moisture content.

In this study, we address these challenges by using NMR and magnetic resonance imaging (MRI) to observe and quantify the specific transport of bound water in wood, while preventing vapor exchange or transport by filling the pores (or voids) with oil. This experimental setup enables us to directly demonstrate that bound water diffuses within the solid matrix of the wood: not through the pores (or voids), but by remaining in the state of bound water and migrating between amorphous regions of the cell walls. Surprisingly, and in contrast to previous assumptions, this diffusion is relatively fast, with a diffusion coefficient comparable to that of bulk water self-diffusion, shows minimal dependence on saturation, and, in strong contrast to free water transport, is independent of the direction of wood. Moreover, the diffusivity varies with temperature following an Arrhenius law. These different elements suggest that bound water transport is an activated process.

II. MATERIALS AND METHODS

A. Materials

Two hardwood species [see Fig. 2(a)] were investigated in this study. Oak samples were collected in the Seine-et-Marne region, France, while poplar samples were collected in the Aisne region, France. Regarding the structures, oak

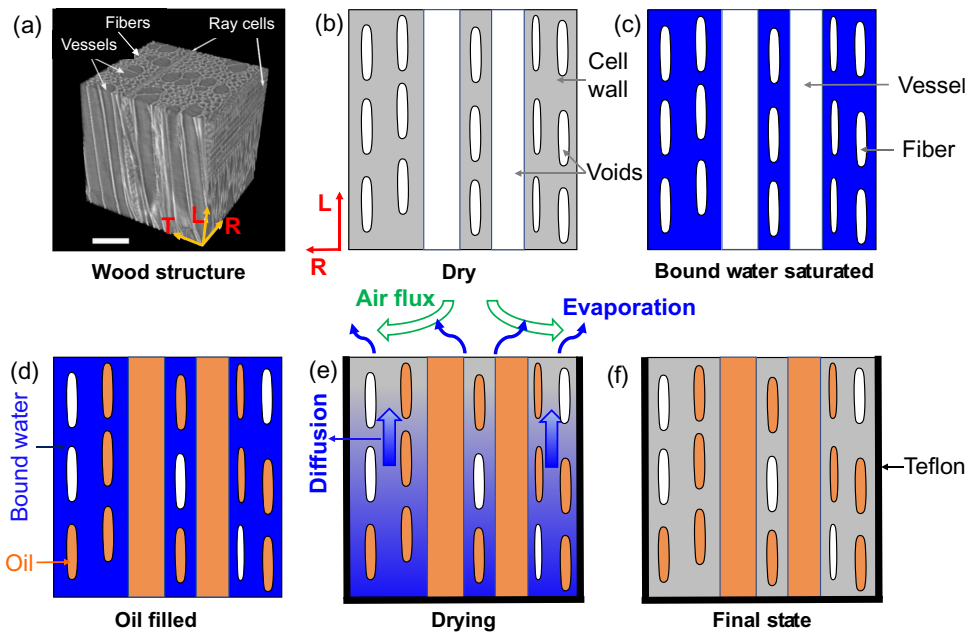


FIG. 2. Principle of the drying test with an oil-filled wood sample. (a) A typical hardwood structure, which consists of voids of various shapes (vessels, fibers, and ray cells, with some tiny connections between them), as shown in a three-dimensional rendering of a synchrotron x-ray micro-computed-tomography image (scale bar 100 μm) [23]. (b) This structure is presented along the longitudinal direction (the main tree axis) in a simplified way, retaining the main porosity including fibers and vessels. (c) After being placed for several weeks at a high relative humidity (close to 100%) the dry sample in (b) is saturated with bound water, which penetrates in the cell walls forming the solid structure. (d) Afterwards, the sample is placed under a vacuum and immersed in oil which fills the accessible pores, leaving some of them empty. (e) The material is subjected to a dry air flux that induces bound water transport inside the solid structure toward the free surface. (f) A dry sample filled with oil after drying in (e). The diffusion of bound water is presented in the longitudinal direction [(e)]; diffusion in the other directions (radial and tangential) may be studied in the same way, leading to a gradient of bound water concentration either transverse or perpendicular to the plane of the scheme in (e). The principle is identical for a softwood sample, although its porous structure is different.

is a ring-porous wood made of up to four rows of solitary large pores in earlywood, the vessel diameter is around 200–250 μm , and the fiber diameter is around 10–20 μm . Poplar, a semidiffuse porous wood, is made of a homogeneous distribution of medium pores (solitary, multiples, and small cluster), with fiber diameter ranging from 5 to 40 μm and vessel diameter of around 110 μm . A softwood, fir, from the Jura region in France, was also investigated. Its porous structure includes tracheids with diameters ranging from 20 to 40 μm , along with a small proportion of rays. All samples were taken from the inner part of the trunk (heartwood) and were sawn along the three principal directions of wood—longitudinal, radial, and tangential—to produce samples of about $10 \times 10 \times 10 \text{ mm}^3$, suitable for insertion into NMR tubes. To characterize the material porosity, samples were immersed in water under a vacuum. The volume fraction of water filling each type of pore in the structure was determined through mass measurements and NMR relaxometry (see the methods and data for oak and poplar in Ref. [24]). For oak, the saturation of the medium with water corresponds to a moisture content (defined as the ratio of water mass absorbed to the dry sample mass) of 26% for bound water, 30% for

water in fibers, and 59% for water in vessels. For poplar, the respective values were 21%, 105%, and 33%. For fir, the maximum moisture contents associated with bound water and free water in the tracheids were 16% and 140%, respectively.

Before the next preparation step, all samples were stored in a sealed desiccator maintained at a relative humidity of 99.9% for several months to ensure saturation with bound water [see Fig. 2(c)]. The reference dry state was established by drying the samples in an oven at 60 $^{\circ}\text{C}$ for one week. Further drying at 100 $^{\circ}\text{C}$ confirmed that the residual moisture content after drying at 60 $^{\circ}\text{C}$ was below 0.5%.

To optimally fill the sample pores with oil, samples saturated with bound water were partially immersed in a silicone oil bath [$\text{SiO}(\text{CH}_3)_2$, Aldrich 378380, viscosity 0.5 Pa s] and placed under a vacuum for up to 30 min. Given the difficulty in predicting the NMR characteristics of oils in wood, several oils differing in composition and viscosity were tested. We selected an oil whose NMR relaxation times were distinctly different from those of bound water in wood, enabling reliable signal separation. Additionally, this oil exhibited a stable NMR signal before and after filling the wood, indicating no interaction or

chemical exchange with the wood matrix. Lower-viscosity oils did not significantly increase the filling efficiency, so we instead used a vacuum system to facilitate oil penetration and extended the filling duration for optimal pore saturation. Subsequently, the sample and oil bath system was placed in a desiccator maintained at nearly 100% relative humidity for several days, allowing further oil penetration and ensuring a homogeneous oil distribution while preserving full saturation with bound water. Despite these efforts, the sample pores were not fully saturated with oil [see Fig. 2(d)]. By comparing the sample mass after filling with the maximum moisture content associated with pores (vessels and fibers for hardwood, tracheids for softwood, pores between fibers for cellulose), the oil filling extents were estimated as follows: 94% for cellulose, 60% for oak, 72% for poplar, and 77 % for fir. This indicates a residual unfilled void volume fraction (i.e., not filled with oil) of 17% for poplar, 19% for oak, and 17% for fir over the whole sample volume. Considering the solid matrix (i.e., excluding oil-filled pores) saturated with bound water, the void fraction was estimated as 30% for poplar and 27% for oak.

At the end of the preparation process, the desired free surface of the sample was cleaned of oil by the brushing of it with a cloth. However, some oil remained in the vessels near the solid elements at the top surface, making it difficult to confirm whether the cell walls at the free surface were completely exposed to air, without any residual oil film. To address this uncertainty, drying experiments were conducted under identical boundary conditions with two samples: one filled with oil and subsequently cleaned, and the other oil-free, with both initially saturated with bound water. From the initial saturated state down to 95% saturation, both samples exhibited identical drying rates, indicating similar boundary conditions during this period, as the drying rate is directly governed by the relative humidity at the sample surface. Beyond this period, the drying rate was influenced by the diffusion within the material, depending on whether the pores are filled with oil. Since the air flux was the same for both samples, resulting in identical relative humidity along the free surface, it was confirmed that the presence of oil in the pores had a negligible effect on the boundary conditions. In other words, the surface cleaning procedure is effective in establishing conditions for bound water evaporation, with the cell walls exposed to air.

Cellulose fiber composites were prepared by compression of disordered natural cellulose fibers (Arbocel BC 200, from Kremer Pigmente), previously placed in a sealed desiccator with relative humidity stabilized at 99.9% for a few months. Before compression, the fibers were loosely placed in a 1.2-cm-diameter tube for a disordered distribution. The samples were then compressed to a specific volume [29], achieving a porosity of 0.58 ± 0.02 . Oil impregnation was then performed by partial immersion of

the samples in a silicon oil bath (Aldrich 378380, viscosity 0.5 Pa s).

B. MRI measurements

MRI has been traditionally used to visualize water content in brain [38] and to study the liquid distribution in porous media [39]. It has also been used to image water imbibition and drainage in wood [40,41]. In this study, MRI was used to investigate poplar samples containing bound water. Following the sample preparation (see Sec. II A), the sample was placed inside the magnet coil, with four lateral faces and the bottom surface sealed with Teflon [see Fig. 3(a)] to ensure one-dimensional (1D) diffusion. A constant dry air flux was then applied above the exposed surface to initiate drying [see Fig. 3(a)]. MRI measurements were performed with a Bruker 24/80 DBX 0.5-T ^1H MRI spectrometer, operating at 21 MHz. Two-dimensional magnetic resonance images [see Fig. 3(b)] were obtained with use of the fast low-angle shot sequence [42], a commonly used gradient-echo sequence that allows for short echo times. In this study, the echo time was set to 2.3 ms, shorter than T_2 of approximately 6 ms for poplar. The field of view was $80 \times 80 \text{ mm}^2$, with 48 pixels in the x direction and 128 pixels in the z direction. A total of 128 scans were accumulated per image. The flip angle was set to 90° , and the recovery time was adjusted to 50 ms,

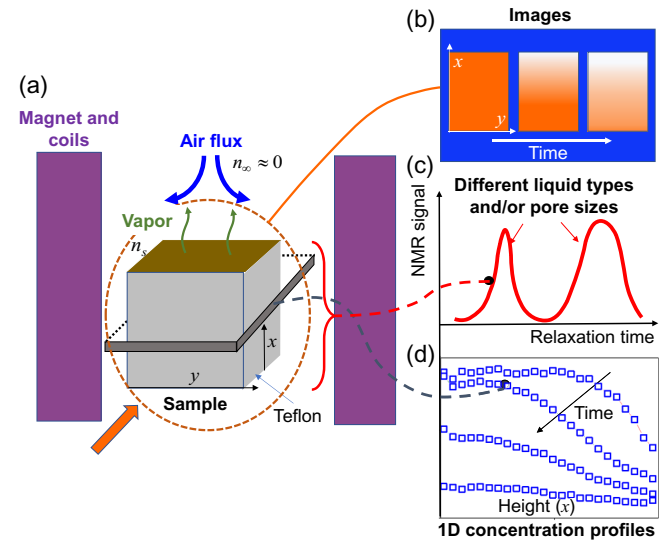


FIG. 3. Principles of NMR and MRI measurements. (a) The sample is placed in the central region of a magnet. Depending on the NMR sequence used (see Sec. II) one can obtain (b) successive images of the water distribution in a two-dimensional plane perpendicular to some direction (orange arrow), providing a qualitative appreciation of the global process characteristics, (c) the probability density function of the relaxation time of the liquid phases in the medium, giving a precise measure of the bound water amount over time, or (d) the 1D distribution of liquid along one axis, providing quantitative information about the in-depth transport of bound water over time.

leading to an acquisition interval of approximately 6 min per image, well below the characteristic timescale of water transport. The slice thickness was 50 mm, which exceeded the actual sample thickness. These parameters were optimized to maximize signal strength despite the progressive decrease in transverse relaxation times (T_1 and T_2) during drying. However, the combination of high flip angle and large slice thickness restricted the analysis to qualitative insights. Each image represents a horizontal projection of the signal across the whole sample thickness in a given direction. Consequently, the pixel brightness reflects the averaged local signal intensity along this thickness, which depends not only on the local moisture content but also on the local relaxation times. As a result, these images provide only a qualitative view of the evolution of water content in the different regions of the sample. Additionally, the spatial distribution of bound water along the sample axis was determined with an original MRI approach, analogous to previous methods developed to distinguish bound water from free water during wood drying [28], but here it was specifically adapted to differentiate bound water from oil within the sample, on the basis of their distinct relaxation times. Specifically, T_2 values for bound water in wood range from 1 to 6 ms, depending on the wood species, and decrease as drying proceeds. In contrast, the T_2 value for silicon oil in filled wood pores in this study is around 230 ms and remains stable throughout the drying process.

The spatial distribution of all liquid molecules along the sample axis [i.e., 1D profiles; see Fig. 3(d)], including both oil and bound water, was measured with use of the single-point imaging sequence [43]. The single-point imaging parameters were set as follows: number of scans 256, signal collecting time 104 μ s, field of view 44 mm, number of pixels 64, flip angle 15°, and repetition time 200 ms. This resulted in a total acquisition time of 54 min. Subsequently, with the same MRI system we measured the T_2 distribution with a multiecho sequence [23] using the following parameters: number of scans 512, echo time 5.22 ms, number of echoes 16, field of view 180 mm, number of pixels 64, and repetition time 2 s. This resulted in a total duration of 17 min. This sequence is sensitive to liquid molecules only with T_2 values larger than a few tens of milliseconds, thus enabling the selective detection of oil. To ensure this, we excluded the first two echoes, where a residual signal from bound water might be present. For the third echo, the signal of bound water was negligible, and a single-exponential fit was used. The bound water distribution was then obtained by subtraction of the oil profiles from the total liquid profiles.

C. NMR measurements

To have quantitative data, NMR relaxometry was used, as it enables the detection of any sufficiently mobile molecules, including a monolayer of adsorbed water

molecules on the solid surface of nanoporous silica glass [44], and enables one to distinguish between different liquid phases within the system.

Specifically, after previous preparation (see Sec. II A), the sides and the bottom of the sample were covered with Teflon [see Fig. 2(e)] to prevent moisture loss through these faces. The sample was then placed in an NMR tube (external diameter 18 mm) with its top surface exposed to air, and the tube was immediately inserted into the NMR coil for measurement. A dry air flux was applied 1.8 cm above the free surface at a rate of 2.5 l/min, resulting in an average boundary layer thickness associated with water transfers of 1.7 mm (see Appendix A). This value was determined in accordance with the procedure described in Ref. [45], by independent experiments on a cellulose fiber stack initially fully saturated with water under identical experimental conditions. By analysis of the boundary conditions, the slope of the saturation versus time curve provided the value of δ .

Drying processes were investigated by ^1H low-field NMR relaxometry with a Bruker minispec NMR spectrometer (18 mm mq20, 0.5 T, 20 MHz). The transverse relaxation time T_2 in the medium was measured with the use of a Carr-Purcell-Meiboom-Gill sequence [46,47], which records the evolution of the NMR signal during spin transverse relaxation following excitation (resonance). The parameters of the Carr-Purcell-Meiboom-Gill sequence were optimized through preliminary tests to balance data quality with time constraints, particularly to capture the broad range of relaxation times observed in such multi-scale porous materials while minimizing the temperature rise due to the NMR sequence itself. Specifically, the NMR sequence was applied 64 times (scan number) according to the phase cycling process, and the data from these runs are averaged over a period of around 4 min, thereby increasing the signal-to-noise ratio. The time interval between successive pulses in a pulse sequence was set as 2 s, ensuring full magnetization recovery, including that of the silicone oil in the pores. The echo time, which is the delay between the 90° excitation pulse and the acquisition of the echo signal between two successive 180° pulses, was set as 0.2 ms, with the number of echoes set as 1500, for capturing best the evolution of the signal of oil and bound water over time during relaxation. In these cases, the total duration for a complete measurement of one T_2 distribution is 4 min, which is significantly shorter than the total duration of the drying process for both wood and cellulose stacks, which exceeds several hours even under the highest temperature in this study. After performing Laplace inversion on the signal by a standard CONTIN processing [48,49], we obtained the probability density function (PDF) of the NMR relaxation time T_2 , which provides insight into the distribution of bound water and other liquid phases within samples at each time point.

During drying, the PDF of water in wood evolves, reflecting changes in the quantity and distribution of different liquid phases within the various pore types of the samples. As long as the same NMR sequence and processing parameters are used, the integral of the PDF under a given peak provides a reliable measure of the liquid mass associated with that specific phase [50]. Although the NMR signal intensity is temperature dependent, each experiment is conducted at a constant temperature. Moreover, we focus on the relative saturation, which is obtained by normalization of the water signal at each time point to the initial value; therefore, temperature variations have no impact on the interpretations of the data.

Experiments were conducted at temperatures ranging from 13 to 50 °C, controlled with a water flow system (see Fig. 4). Water at the target temperature was circulated around the sample inside the spectrometer tunnel. More precisely, heated or cooled water flowed through a spiral-shaped channel in the tube above the sample and returned via a similar intertwined channel. This setup, enclosed with the NMR spectrometer tunnel, allowed precise control of the sample environment and maintained a localized temperature distinct from that of the ambient air outside the spectrometer. A dry air flux was injected through a narrow tube passing in the middle of the spiral-shaped channels, allowing it to equilibrate with the surrounding water temperature before reaching the sample region. Although the precise temperature distribution within the system was not controlled, the final temperature in the chamber was monitored with a type T thermosensor made of constantan alloy, placed at the edge of the top surface of the sample (see Fig. 4). This sensor provided an estimate of both the sample surface and the air flux temperatures. Given the confinement of the chamber, topped by the water circuits

and continuously ventilated by the air flux, and the long duration of the experiments (typically several hours), it can be reasonably assumed that the entire sample reached a temperature close to that recorded by the sensor after an initial transient phase. In practice, the sample was introduced at ambient temperature, and the water flow was gradually adjusted to reach the target temperature. Additionally, a cryostat system used to cool the NMR coil region (see Fig. 4) could also be tuned to assist in temperature stabilization. The initial adjustment to the target temperature took only a few minutes, which is insignificant compared with the full duration of the drying process and has negligible impact on the data.

III. RESULTS AND DISCUSSION

We first used MRI to trace the evolution of a simple wood sample (i.e., without oil) initially saturated with bound water and subjected to a dry air flux along its top surface (see Sec. II B). The MRI sequence allows imaging of the bound water, which produces a lower signal intensity than free water [see Fig. 5(a)]. As drying progressed, the signal associated with bound water gradually diminished [see Fig. 5(b)]. Notably, this process occurred across the whole sample thickness rather than forming a dry front progressing from the top surface [see Fig. 5(b)]. This behavior is reminiscent of a diffusion process, likely driven by bound water transport inside the structure and toward the evaporative surface. While this experiment illustrates bound water transport within the structure, vapor transport and both adsorption and desorption mechanisms cannot be excluded in the moisture transport due to the presence of open pores.

To isolate the specific transport of bound water within the solid phase, we imaged the drying process of a wood sample initially saturated with bound water, while its accessible pores (see Fig. 2) was filled with oil (see Sec. II B), thereby significantly limiting free water or vapor transport through its pores. The sample was prepared to ensure boundary conditions corresponding to cell walls saturated with bound water and exposed to air at the free surface. In this case, both oil and bound water contribute to the NMR signal. To obtain an image of the bound water distribution, the oil signal obtained at the end of the drying process was subtracted from the images. Under these conditions, it was observed that bound water again progressively disappeared over time and across the entire sample thickness at each time point [see Fig. 5(c)]. These observations confirmed that a diffusion process occurs specifically for the bound water within the cell wall structure.

For technical reasons (see Fig. 5 and Sec. II B), these images of bound water remain somewhat qualitative. However, NMR measurements (see Sec. II C) enable us to quantitatively extract the evolution of molecular fractions

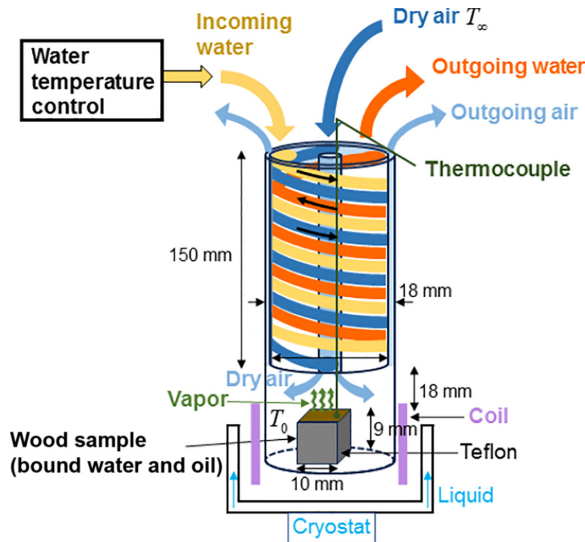


FIG. 4. Principle of the setup inserted in the NMR magnet for controlling the temperature during a drying test.

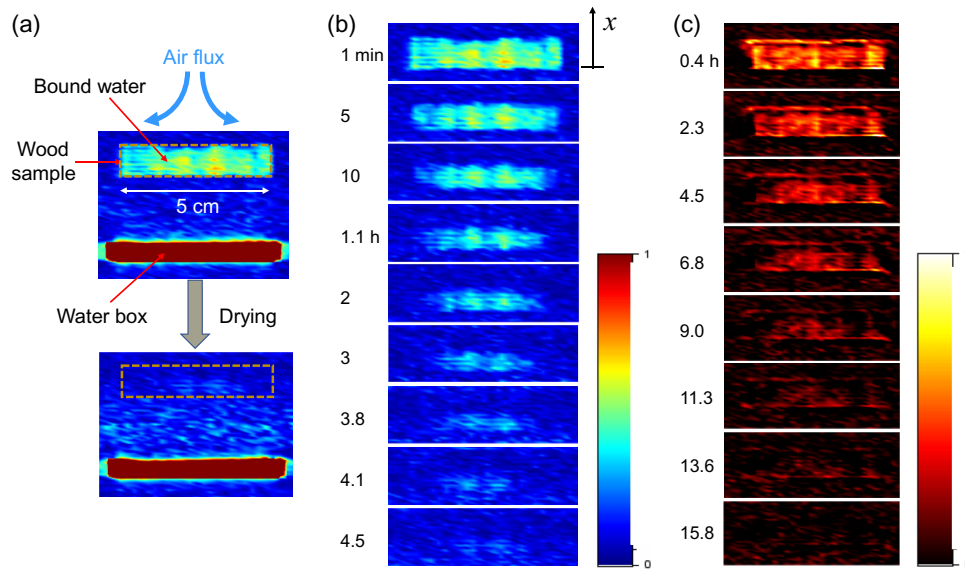


FIG. 5. Drying at ambient temperature of a square poplar sample. (a) The sample was initially saturated with bound water (no free water) and subjected to a dry air flux along its top surface. (b) Views from MRI at different times during the process for a sample with empty pores. (c) Views from MRI at different times during the process for a sample with pores filled with oil. The signal intensity in the images is represented by a color scale (on the right) going from 0 (no signal) to 1 (bulk water). An airtight box [in (a)] filled with water is placed below the sample to serve as a reference for the images. The images correspond to the total water signal along the sample thickness (perpendicular to the image plane), each elementary signal being possibly weighted by the local relaxation, an effect that tends to enhance the decrease of the apparent signal bound water amount when the saturation decreases. The initial inhomogeneities of signal are mainly due to the anisotropy (growth rings) of the sample density in the transverse direction.

through the PDF of sufficiently mobile molecules containing protons (see Fig. 3 and Sec. II C), providing a straightforward view of the temporal evolution of oil and water phases within the material. Throughout the measurements on both hardwood and softwood samples, qualitatively similar results were obtained despite structural variations,

particularly in pore distribution. Comparable trends were also found in cellulose fiber stacks, confirming the generality of the observed behaviors.

For a dry sample filled with oil [see Fig. 2(f)], the PDF exhibits a single peak at 230 ms [see Fig. 6(a)]. For a sample saturated with bound water but free of oil [see

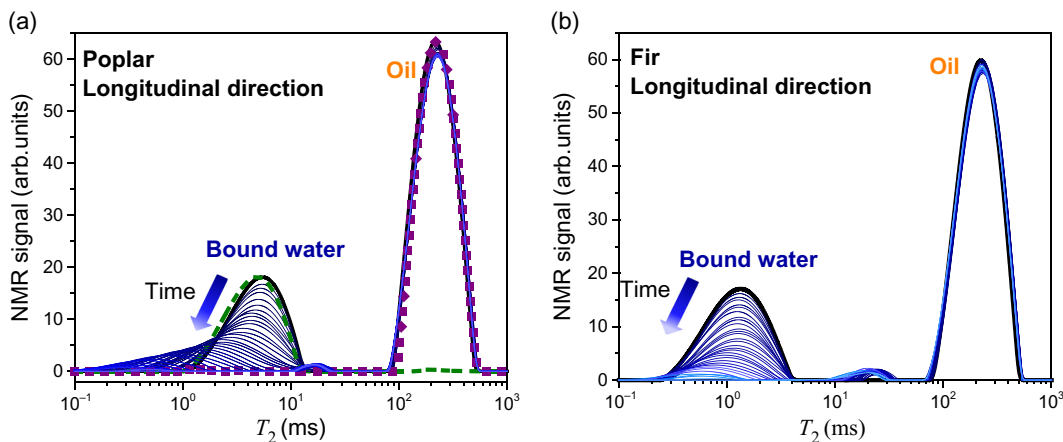


FIG. 6. Probability density function of the transverse relaxation time of bound water and oil at successive times (downwards) during drying at ambient temperature. The thick black line corresponds to the initial state. (a) In poplar samples. (b) In fir samples. In (a) the dotted purple line corresponds to the case of oil filling a dry sample, i.e., without any type of water, and the dashed green line corresponds to the case of a bound water sample without oil. Note that from additional tests it is proved that the peak of very small amplitude at around 20 ms corresponds to a very thin layer of oil appearing between the Teflon tape and the sample.

Fig. 2(c)], the PDF also exhibits a single peak, although at a significantly smaller T_2 value [see Fig. 6(a)]. The position of this peak varies between 1 and 6 ms depending on the wood type. Finally, a sample saturated with bound water and with pores filled with oil [see Fig. 2(e)] exhibits two peaks, corresponding to bound water alone and oil alone in the sample, respectively (see Fig. 6). These results demonstrate that even in oil-filled wood, bound water can be accurately detected, despite primarily existing as molecules dispersed within the solid structure and interacting with cellulose through hydrogen bonds. Note that independent tests also prove that the bound water amount not detected by such NMR measurements is negligible (see Sec. II C).

Afterwards, we focus on the case of a wood sample saturated with bound water and with pores filled with oil, exposed to a dry air flux [see Fig. 2(e)]. The amplitude of the bound water peak continuously decreases during the process, indicating a progressive loss of bound water (see Fig. 6). In contrast, the oil peak remains nearly unchanged, confirming that all the oil remains confined within the sample. Moreover, the persistence of two distinct peaks associated with two different relaxation times indicates no mixing of the two phases, confirming that there is no significant exchange between them [51]. This NMR measurement thus clearly proves that the bound water manages to escape from the wood sample, even though the accessible pores are filled with oil. A simple experiment confirms that this behavior cannot be attributed to the diffusion of water molecules through oil: under identical experimental conditions, a water volume covered by a 1-mm-thick oil layer remains unchanged over several days. These observations, consistent across both major wood types exhibiting different structures (hardwood and softwood) [see Figs. 6(a) and 6(b) and Appendix B], lead to the fundamental conclusion that the bound water is transported through the solid phase, specifically within the cell walls.

MRI measurements using two sequences (see Sec. II B) provide further insight into this transport process. By subtracting the oil distribution from the total liquid distribution, we obtained the spatial bound water distribution in each cross section along the sample axis (see Sec. II B). Although the data exhibit notable scatter due to the cumulative uncertainty inherent in this multistep process (see Fig. 7), clear qualitative trends emerge. The bound water, initially distributed homogeneously throughout the sample [see Figs. 2(e) and 7], progressively diminishes during drying. The concentration starts to decrease from the top surface, forming a gradient toward the sample interior. Then the bound water content continuously decreases throughout the entire sample until complete drying is achieved (see Fig. 7). This behavior indicates that the water molecules spontaneously move toward regions of lower concentration, i.e., they diffuse through the solid structure. More precisely, since the

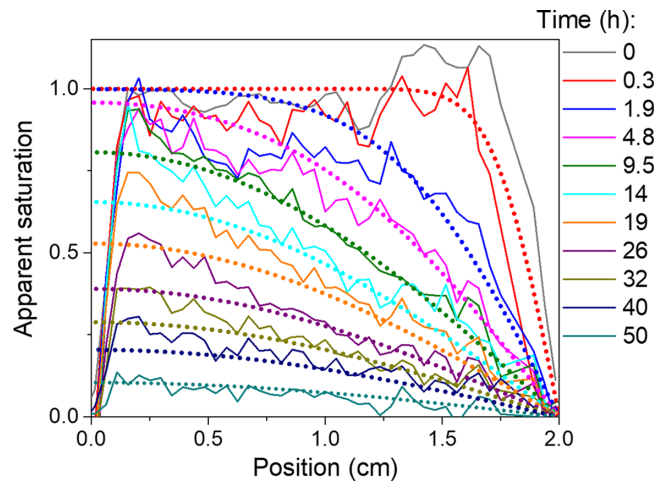


FIG. 7. 1D bound water distribution (continuous lines) measured by MRI at different times during drying at ambient temperature (23 °C). This experiment was conducted on a poplar sample filled with oil (continuous lines). The predictions of the model (with $D = 1.7 \times 10^{-9} \text{ m}^2/\text{s}$) at the same times are shown as dotted lines of the same colors. Note that for the model fitting the saturation has been assumed to correspond to the average value of the water content in the initial state.

pores are occupied by oil, this observation confirms that bound water diffuses along the solid structure but inside the solid phase, i.e., without any exchange (sorption or desorption) with external phases such as free water or vapor.

Since the bound water extraction is a diffusion process, it can be analyzed in more detail. In the case of a simple, homogeneous material with a constant diffusion coefficient, i.e., one that is independent of the local saturation (defined as the ratio of the current water content to the maximum water content), the process can be completely described by classical diffusion theory [52]. Specifically, the transport of bound water follows a simple diffusion equation:

$$\frac{\partial s}{\partial t} = -D \frac{\partial^2 s}{\partial x^2}, \quad (1)$$

where D denotes the effective diffusion coefficient of bound water through the material. Considering the boundary conditions, there is no mass transfer through the sample bottom, while at the top surface, the internal flux equals the external flux imposed by the dry air flux along the interface [45]:

$$-\rho_s S_m D \frac{\partial s}{\partial x} = -\frac{\rho_0 D_0}{\delta} (n_\infty - n_s), \quad (2)$$

where n_s is the relative humidity along the interface, n_∞ is the ambient relative humidity, ρ_0 is the saturation vapor density, D_0 is the diffusion coefficient of the vapor in air,

which is temperature dependent, ρ_s is the density of the dry sample, S_m is the maximum moisture content (the bound water to dry mass ratio) in the sample, and δ is the characteristic thickness of the boundary layer for vapor diffusion (see Sec. II C and Appendix A). Assuming sorption equilibrium ($s = f(n)$, where f is the desorption curve, i.e., the relation between the moisture content and the relative humidity at equilibrium during desaturation; see Appendix C for details) at the sample surface subjected to a constant air flux, the above boundary condition can be transformed into an equation involving only s , and Eq. (1) can be solved (see Appendix D).

This approach enables the prediction of the evolution of the saturation distribution along the sample thickness over time up to complete drying based solely on the knowledge of the diffusion coefficient D . In this context, the 1D profiles obtained by MRI (Fig. 7) can be approximately reproduced by adjustment of the value of D to a given constant. A more straightforward estimation of D can be obtained by fitting the average saturation versus time curves (see Fig. 8), which are derived from the integration of the NMR signal under the peak of bound water in the PDF (see Fig. 6). In this context, the data show good reproducibility (see Fig. 13). Remarkably, in some experiments, a single diffusion coefficient appears to be sufficient to well describe the drying behavior over the entire saturation range (Fig. 8), with less than 10% uncertainty in the time required to reach a given saturation level. Given that the evolutions of the diffusion processes are similar when the time is rescaled by l^2/D (with l the sample thickness), this uncertainty in time directly translates into an equivalent uncertainty in the diffusion coefficient.

However, in most cases, deviations from the constant-diffusion model appear for saturation exceeding 0.7, with discrepancies reaching up to a factor of 2 at the highest saturation levels [Fig. 8(b)]. In summary, while a simple diffusion model with a constant diffusion coefficient effectively captures the data for saturation levels below 0.7, a slower diffusion process may be observed at higher saturation.

Therefore, contrary to the usual conclusions drawn from global measurements of moisture transport in cellulosic materials with open porosity, and contrary to the common assumption in that field [13,53–55], as well as contrary to experimental observations [56] and molecular simulations [57] of self-diffusion coefficients, the transport diffusion coefficient of bound water does not exhibit a significant dependence on saturation. Moreover, the slight decrease observed with increasing saturation is opposite the widely reported trend of increasing self-diffusion in cellulosic materials.

Note that this result may appear to contradict the observed decrease in T_2 when the saturation decreases (see Fig. 6), which *a priori* reflects an increase of the confinement, possibly associated with a decrease of mobility. More precisely, a decrease in T_2 reflects a variation of the fractions of time spent by the molecules in different environments [50], which here might be either a direct contact with a cellulose molecule or an immersion among a few other water molecules, where the relaxation would be longer. From this description, we anticipate that the fraction of water molecules in direct contact with the solid (cellulosic) structure increases when the saturation decreases, leading overall to a reduction in the average

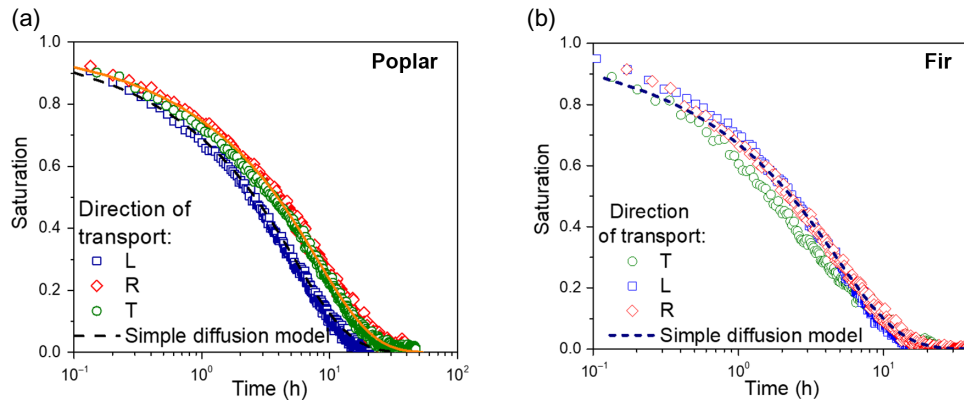


FIG. 8. Saturation over time during the drying of oil-filled wood samples along different surfaces. This leads to transport in different directions at ambient temperature. (a) For poplar. (b) For fir. The lines illustrate examples of the simple diffusion model specifically fitted to poplar data with diffusion coefficient $D = 1.7 \times 10^{-9} \text{ m}^2/\text{s}$ (longitudinal direction, in black) or $D = 1.1 \times 10^{-9} \text{ m}^2/\text{s}$ (radial or tangential direction, in orange) and to fir data (radial direction) with $D = 2.3 \times 10^{-9} \text{ m}^2/\text{s}$. In the latter case, a fit of the model to the data in the other directions leads to diffusion coefficient differing by less than 20% from this value. Note that due to the effect of the remaining voids partly balanced by the effect of tortuosity of the solid phase, the bound water diffusion coefficient D_b inside the solid phase, is close to the value measured for D . L, longitudinal; R, radial; T, tangential.

distance between liquid-solid interfaces. However, there is no direct correspondence with the macroscopic mobility of water molecules through the structure: for example, the description above would be the same and would lead to almost the same quantitative prediction for T_2 in the case of initially enclosed (disconnected) pores and in the case of connected pores, whereas the mobility and thus transport of water through the porous structure in the case of enclosed pores would be impossible for disconnected pores. Furthermore, within the frame of the interpretation of the origin of diffusion of bound water in such systems (see below; i.e., an activated process) it is not clear how the distance between liquid-solid interfaces can impact the diffusion rate.

This slight decrease with increasing saturation mentioned above can be explained by the presence of some voids (not filled with oil) in the cell wall structure. Although these inclusions are, in principle, enclosed by the surrounding solid matrix or by oil films, they may still contribute to water transport, as vapor can diffuse through them during drying. Specifically, some voids may contain air and vapor due to the ongoing exchange between vapor and bound water, and the vapor can be extracted from a cell wall, then diffuse through an adjacent inclusion driven by a concentration gradient, and then re-enter another cell wall. In this context, the homogenization theory can be used to estimate the impact of these inclusions on the overall water transport within the structure (see Appendix E).

In this study, considering the fraction of voids remaining unfilled after oil imbibition (see Sec. II A), the fraction of voids in the solid matrix (including the dry solid and the bound water) was approximately 27% for oak, 30% for poplar, and 23% for fir. Under these conditions, at ambient temperature, the effective diffusivity is expected to be about 0.8 times the diffusivity in the solid matrix for $n > 0.8$ and 1.4 times the diffusivity for $n < 0.8$ (see Appendix E). These values provide a reasonable explanation for the observed discrepancy between the constant-diffusion model and the data at high saturation; however, a comparison with greater precision remains infeasible. Specifically, our analysis focused on the average saturation (Fig. 8), whereas, due to the nature of diffusion, the bound water saturation along the transport direction is not homogeneous. Additionally, the precise spatial distributions of the residual voids across different samples were not controlled.

This analysis supports the validity of assuming a constant bound water diffusion coefficient in the solid matrix, i.e., a value independent of saturation. It finally leads to the conclusion that the variation of the transport diffusion coefficient of bound water remains nearly constant. However, as a corollary of the above analysis, we note that the constant diffusion coefficient derived as described above overestimates the actual bound water diffusivity in the solid by a non-negligible factor, which depends on

both temperature and the diffusion coefficient in the solid (see Appendix E). For simplicity, we retain the constant-diffusion model fitted primarily to the low saturation range (below 0.8). For the physical interpretation of the data, however, we correct this value by the factor estimated from the homogenization theory (see Appendix E and Fig. 12). In practice, this correction involves dividing the apparent coefficient by a factor decreasing from about 1.75 to 0.9 when the temperature increases from 10 to 50 °C. This variation in the correction factor arises from the changes in the relative values of bound water diffusivity and vapor diffusivity with temperature.

To approach the effective diffusion coefficient of bound water in the solid matrix, which is denoted as D_b , an additional correction must be applied to account for the presence of inclusions filled with oil in the medium. This is usually expressed in terms of the tortuosity, which represents the ratio between the average path length that water molecules must follow through the structure (avoiding inclusions) and the direct geometric distance (in the absence of inclusions). The diffusivity found from our tests corresponds to the effective diffusion coefficient of the medium divided by this tortuosity factor. Although a precise evaluation of the tortuosity requires detailed information on the shapes and spatial distribution of these inclusions, we can consider the estimation of the tortuosity for a sphere packing (i.e., around $\pi/2$, since the paths have to essentially circumvent spheres) as an upper bound. In the case of poplar, the concentration of inclusions is 43%, which is significantly lower than for a sphere packing (i.e., 74% in a crystalline configuration). On the basis of this, a reasonable estimate for the tortuosity is approximately 1.3. Accordingly, the effective transport diffusion coefficient of bound water in wood cell walls can be deduced by multiplying the measured apparent diffusivity by this factor.

A remarkable point is that the diffusion coefficients obtained from our measurements (see Fig. 8) are of the same order as the self-diffusion coefficient of water in the liquid state ($2.3 \times 10^{-9} \text{ m}^2/\text{s}$ at ambient temperature), although bound water is not in a condensed state but is dispersed in pools containing at most a few molecules (see Fig. 1). Furthermore, one might consider that the mobility of bound water is restricted by the solid matrix. Given this high diffusivity, the term “bound” appears rather misleading. As a consequence, bound water diffusion relies on a distinct but highly efficient physical mechanism.

Another noteworthy observation is that the diffusion of bound water in wood appears essentially independent of the direction. In this study, drying tests were conducted by application of the same dry air flux along the different faces of the oil-filled wood samples, thereby inducing water transport inside the sample along different directions—longitudinal, radial, or tangential—all

under identical boundary conditions. The resulting saturation versus time curves were found to be approximately identical across all three transport directions (see Figs. 8 and Appendix F) for all wood types, except for poplar in the longitudinal direction, where the diffusion coefficient fitted by the model was about 1.5 times greater than in the other directions [see Fig. 8(a)]. These three principal directions, i.e., longitudinal, which is along the vessel's axis, tangential, which runs parallel to the growth rings, and radial, which is perpendicular to the growth rings (see Fig. 2), reflect the pronounced anisotropy of wood. The pore morphology and connectivity vary significantly across these different directions, and some degree of alignment of cellulose or hemicellulose fibers along the longitudinal direction in the cell walls is expected. This finding contrasts with the usual appreciation from global vapor transfer measurements in wood with open pores [55,58] and the penetration dynamics of free water in wood [24], which typically show that moisture transport is significantly dependent on the direction. However, in those previous studies, the vapor or liquid flow through the anisotropic porous structure significantly contributes to the overall moisture transport, making the transport dependent on the material anisotropy. Therefore, differences in the diffusion properties across directions are naturally observed. In contrast with all previous studies, the present study isolates and quantifies the bound water transport exclusively, so that bound water strictly travels through the solid phase, specifically through the amorphous regions between the microfibrils. The absence of

directional dependence indicates that, at the molecular scale, the diffusion pathways, which are along the amorphous regions between microfibrils, are well-connected and exhibit minimal variation with the direction. These regions have been reported to be structurally disordered and isotropic, with no preferred orientation [57,59]. This, in particular, implies that the tortuosity of the network of amorphous regions, which has to circumvent obstacles formed by the crystalline regions and the oil or air inclusions, remains relatively uniform across different orientations. Note that this observation strongly contrasts with a cellulose fiber stack for which the fibers are in contact through only a few dispersed points so that the water has to follow very different paths depending on the mean transport direction [29].

A final noteworthy characteristic of bound water transport in wood is the variation of diffusivity with temperature. By integrating a heat control system inside the NMR spectrometer (see Fig. 4 and Sec. II C) and imposing a dry air flux at the same temperature as the sample, we were able to directly monitor the diffusion process during drying. For each temperature, a single diffusion coefficient was found to properly describe the process across the whole range of saturation. It was observed that drying at different temperatures can be effectively described by a simple diffusion process, with the process accelerating as temperature increases [see Fig. 9(a)], leading to an increase in diffusivity with temperature. This increase is rapid, approximately a factor of 6 over a temperature range of 30 °C, which is considerably larger than

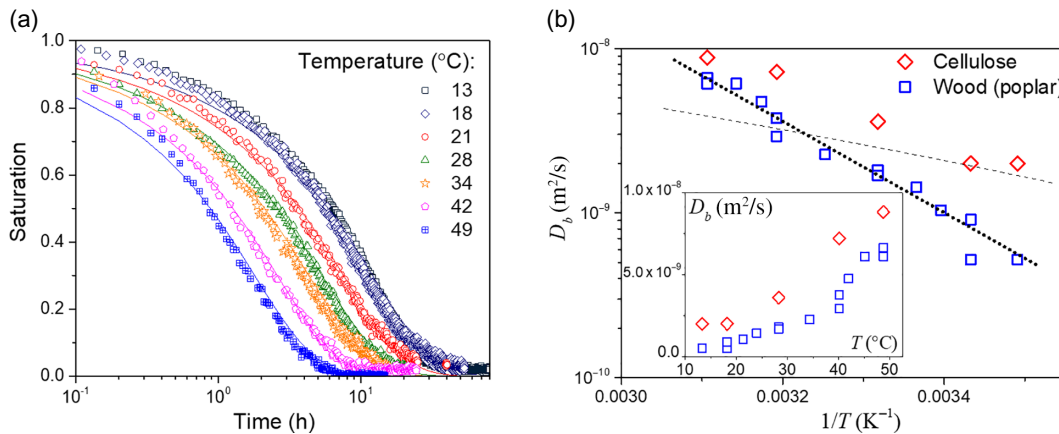


FIG. 9. Bound water diffusion during drying at different temperatures. (a) Saturation vs time curves during poplar drying along the longitudinal direction at different temperatures. The continuous lines correspond to the diffusion model fitted to the data. (b) Bound water diffusion coefficients in the solid phase as a function of the inverse of the temperature for wood (after corrections indicated in the text) and cellulose. For cellulose, we present the diffusion coefficient within the fibers, derived from data for the cellulose fiber stack, obtained with the model in Ref. [29]; therefore, these data are *a priori* intrinsic to cellulose fibers, i.e., they are independent of the porosity or structure of the fiber stack. The inset illustrates the same data as a function of the temperature. The dashed line corresponds to the self-diffusion coefficient of pure water according to a semiempirical model fitted to reference data (see Ref. [64]). The dotted line is a straight line fitted to data for wood.

the increase of the self-diffusion (typically by a factor of about 2 [see Fig. 9(b)]) over the same temperature range. This finding further underscores the specificity of bound water transport in wood, which differs significantly from the flow or diffusion in a standard liquid phase. Note that the increase of the diffusion coefficient with temperature may be well described by an Arrhenius law [see Fig. 9(b)], i.e., $D_b = D_\infty \exp(-\omega/k_B T)$, where T is the temperature, $k_B = 1.38 \times 10^{-23}$ J/K is the Boltzmann constant, $D_\infty = 2.8 \text{ m}^2/\text{s}$, and $\omega/k_B = 6400 \text{ K}$ is a characteristic activation energy. Such an Arrhenius variation has generally been assumed or observed in the characterization of the global diffusion of vapor through wood with open porosity [60–63]. However, unlike to all previous studies, our value corresponds solely to the transport diffusion of bound water.

The generality of these transport characteristics of bound water in cellulosic materials is confirmed by similar experiments conducted on cellulose fiber stacks. A single diffusion coefficient is sufficient to rather well represent the saturation versus time curve (see Appendix G), with a diffusivity depending on the geometry of the fiber network [29]. Nevertheless, it must be noted that some discrepancies emerge at saturation above 0.9, indicating a slight decrease in the bound water diffusion coefficient at very high saturation, which might be superimposed on the effect observed with wood samples. This diffusion coefficient varies roughly with the temperature in the same way as in wood [see Fig. 9(b)].

The diffusion behavior of bound water in wood and cellulosic materials suggests that it is an activated process as for diffusion in solids [65] or in liquids [66]. Given that bound water is adsorbed within the nanoporous structure of the cellulosic fibers, it is reasonable to describe the diffusion process as an interstitial diffusion [67] where the molecules move from one adsorption site to another by successive adsorption and relocation steps. In this context, a simple description is an intermittent Brownian motion as follows. We assume that, per unit time, a water molecule has a probability p of escaping from their position. When it escapes it makes an elementary jump of average length ϵ . The escape probability is then $p = v \exp(-\omega/k_B T) \approx 1/\theta$, in which v is the vibration frequency of the adsorbed molecules and ω is an activation energy barrier that the molecule has to overcome to escape from the adsorption site. In general, a water molecule will jump from one site to another without escaping from the fiber as vapor, implying that ω should be less than the energy of sorption or desorption though likely of the same order of magnitude. Consider the transport along a given direction x . At each time, the molecules can escape from their position and move in either direction along the x axis with equal probability. Consequently, when the concentration of molecules (number of molecules per unit volume) $c(x)$ is uniform, an equal number of molecules cross a given surface in the two

opposite directions at each instant, resulting in no net transport. However, when a concentration gradient is present, the situation changes. The flux through a surface of area S and situated between x and $x + \epsilon$ arises from molecules escaping from a layer of thickness ϵ around x , and moving toward larger x , as well as from molecules escaping from a similar layer around $x + \epsilon$, and moving toward smaller x , both with equal probability. Thus, the net flux is $S\epsilon(c(x) - c(x + \epsilon))p$, which can also be written as

$$\Phi = -D_b \frac{\partial c}{\partial x},$$

where $D_b = p\epsilon^2$.

This model aligns with the various diffusion characteristics observed in the experiments: (1) diffusion coefficient independent of the saturation, (2) diffusion process independent of the organization of the sites (and thus of the material structure), only the gradient of concentration playing a role, and (3) diffusion coefficient following a model close to an Arrhenius law. Remarkably, it was found that the energy barrier ω of this model (i.e., $\omega \approx 6400k_B$) corresponds to an energy of 53 kJ/mol, close to the heat of vaporization of water 45 kJ/mol, which is expected to be slightly smaller than the heat of desorption [9,68]. Along their path, the molecules encounter energy barriers of various levels; however, the limiting ones for a collective transport are the largest barrier. Consequently, this similarity between the activation energy and the sorption energy suggests that, somewhere along the path of diffusion, the water molecules nearly return to the vapor state, possibly by jumping in an empty void.

It is worth noting that the simple model described above ignores collective effects, i.e., the self-diffusivity D_0 and collective diffusivity D_c are identical. More specifically, for self-diffusion, the path of a molecule is a random walk of successive steps of length ϵ with frequency p , so the mean square displacement covered after time t , associated with the number of steps pt , is equal to $\epsilon\sqrt{pt}$. This again leads to a self-diffusion coefficient $D_0 = \epsilon^2 p$. Collective effects arise from the mutual interaction between neighboring adsorbed molecules, leading to a distinction between self-diffusivity and collective diffusivity.

Collective diffusivity D_c is closely related to the transport diffusivity we estimate by NMR measurements and MRI: $D_b = \Gamma D_c$, with $\Gamma = (\partial \ln(n)/\partial \ln(s))_T$ the Darken factor [67] ($\Gamma = 1$ for a linear adsorption isotherm). Although self-diffusivity and collective diffusivity in nanoporous media are sometimes similar [69], this does not appear to be the case for bound water in wood or cellulose. The limited available data obtained by NMR measurements with the use of a pulsed field gradient sequence that directly characterizes self-diffusion [56,70–72], or from quasielastic neutron scattering [1] provide self-diffusivity estimates much lower than the transport

diffusivity observed in this study, typically on the order of 10^{-10} m²/s at saturation and ambient temperature. Even smaller values were obtained from molecular simulations [57], and a significant reduction of this coefficient as saturation decreases was observed [56,57,68], an effect assumed to be due to a variation of the activation energy with water content [68]. Accordingly, our results suggest that the collective contribution to the transport diffusivity is significant in the case of bound water in wood or cellulose.

Collective effects for diffusion remain little explored in comparison with self-diffusion mechanisms. In particular, the Arrhenius-type temperature dependence and the independence from saturation are notable. Bound water self-diffusivity in biopolymers exhibits a similar temperature dependence, with activation energies of a few tens of kilojoules per mole, but varies strongly with water content [68]. Given that the magnitude of the transport diffusivity observed in this study is at least several times higher than the existing estimates of self-diffusivity, collective effects are dominant, which could be attributed to the existence of percolating bound water pathways within the nanoporous structure, facilitated by the deformability of the polymer matrix [68]. Direct microscopic observations of the geometric structure that could confirm this hypothesis and further elaborate on the origin of water mobility remain unavailable; nevertheless, structural insights can potentially be accessed through molecular simulations [3,73]. Alternatively, the transport diffusion of bound water can be measured via neutron scattering using coherent scattering, while self-diffusion can be assessed through incoherent neutron scattering [67,74]. To the best of our knowledge, this approach has not yet been applied to investigate bound water diffusion in wood.

IV. CONCLUSIONS

The observations reveal that the diffusion coefficient of bound water is independent of its concentration and direction, despite the pronounced anisotropy of wood, and varies exponentially with the inverse of the temperature. These findings demonstrate that bound water transport is an activated process, analogous to the diffusion in solids, with an activation energy comparable to the latent heat of liquid water evaporation, having notable practical implications. It is noteworthy that, at first glance, the diffusion of bound water appears paradoxical, exhibiting both a solid-like character and a relatively high diffusion coefficient. However, this apparent contradiction reflects the unique characteristics of bound water: (1) the diffusion of water molecules embedded within the solid matrix formed by the cellulose molecules, where their motion is thermally activated and governed by the interactions (hydrogen bonds) between the water molecules and the solid matrix; (2) a network of water molecules in the amorphous regions (see Refs. [3,73]) that is significantly denser and more

interconnected than in typical solids, enabling a relatively rapid transport diffusion.

This implies that water can climb up to considerable heights in the form of bound water, as the gravitational potential energy is significantly smaller than the activation energy. Specifically, the activation energy of a molecule, $\omega \approx 21k_B T$, exceeds the gravitational potential energy of a water molecule, $\mu = M_w g h / N_A$, with $M_w = 0.018$ kg/mol representing the molar mass of water, g the gravity acceleration, and $N_A = 6.022 \times 10^{23}$ mol⁻¹ representing Avogadro's constant. As long as the height h reached remains below $21RT/M_w g \approx 3 \times 10^5$ m (with $R = k_B N_A = 8.31$ J/K mol), bound water transport is not constrained by gravitational forces relative to the actual length of the cellulosic material or plant.

The results imply that moisture transport in the form of bound water can occur spontaneously over long distances in any direction within wood or other plant structure, regardless of whether the voids are closed, empty, or filled with a nonaqueous liquid, provided a local bound water deficit exists. This indicates that in plants or trees with a water deficit, where the pores (vessels, fibers, tracheids) are partially empty, and thereby capillary water transport is hindered, bound water transport continues to supply water throughout the entire plant system, albeit at a slow rate.

Conversely, a drying process generally does not lead to the complete removal of moisture of all regions. Because of the diffusion of bound water, a small residual amount of water remains throughout the material until the final stage, when the sample is fully dry. This also implies that the only effective way to prevent bound water penetration in wood, thus limiting the swelling or shrinkage, is to cover the wood surface with an impermeable layer. Simply filling the pores with oil or polymeric material is insufficient.

Given that wood species from various climates share the same fundamental components, i.e., a porous structure with the solid phase (cell walls) composed of cellulose, hemicellulose, and lignin, in differing proportions, similar qualitative transport by diffusion within the cell walls can be expected. However, the variations in diffusivity among different wood types, such as those observed in the current study for oak, poplar, and fir, are not readily explained. A more systematic investigation is required to elucidate the underlying causes of these differences.

In practice, the detailed characterization of the specific diffusion of bound water inside the solid network enables a comprehensive description of moisture transport under hygroscopic conditions in wood (with air-filled pores). In this scenario, vapor diffusion occurs through the porous structure and bound water diffusion occurs within the solid network, with exchanges occurring between the two phases through sorption and desorption processes. Once the diffusion coefficient of bound water is determined, the vapor diffusion coefficient can be derived from steady-state transfer experiments (as demonstrated for cellulose fiber

stacks [31], facilitating a complete description of the transport behavior under diverse conditions. Ultimately, this approach will enable predictions of the drying characteristics of wood based on independent physical measurements.

ACKNOWLEDGMENTS

This work was funded by the China Scholarship Council and co-funded by the European Union (European Research Council PHYBBIOMAT—Grant No. 101095764).

The views and opinions expressed are those of the authors only and do not necessarily reflect those of the European Union or the European Research Council. Neither the European Union nor the granting authority can be held responsible for them.

R.S.-B., L.Y., P.C., and B.M. conceptualized the study. R.S.-B., L.Y., B.M., and J.G.-R. developed the methodology. L.Y. and W.B. conducted the investigation. L.Y. and P.C. performed the visualization. P.C., L.B., and R.S.-B. supervised the work. L.Y. and P.C. wrote the original draft. All authors reviewed and edited the manuscript.

The authors declare that they have no competing interests.

DATA AVAILABILITY

The data that support the findings of this article are not publicly available upon publication because it is not technically feasible and/or the cost of preparing, depositing, and hosting the data would be prohibitive within the terms of this research project. The data are available from the authors upon reasonable request.

APPENDIX A: BOUNDARY LAYER THICKNESS DETERMINATION

The boundary layer induced by air flow induces a boundary layer for vapor diffusion. This boundary layer thus depends only on the flow characteristics along the solid surface, i.e., and not on some properties of the material (see Ref. [45]). A complete similarity analysis of the fluid mechanical problem shows that the total vapor flux perpendicular to the sample surface can be expressed as $j = \rho_0 D_0 (n_s - n_\infty) / \delta$, where n_∞ is the relative humidity of the incoming dry air flux, i.e., $n_\infty = 0$, n_s is the relative humidity along the sample surface, and δ is a function of several dimensionless quantities characterizing the dynamics and thermal properties of the air flux [75]. To determine the value of δ , we used the same setup as that used in our drying experiments, under the same conditions, but replaced the sample with a cellulose fiber stack filled with water (free and bound) of identical height. Then a linear relationship between the saturation and time is obtained, with the slope of the curve $-\partial s / \partial t$. The total vapor flux (per unit area) along the sample surface is given

by $j = -m_{\text{dry}}(\partial s / \partial t) / A$, where A is the area of the sample or water surface and m_{dry} is the dry mass of the sample. In this case, with a wet porous medium, the humidity at the sample surface remains at its maximum value (i.e., $n_s = 1$) because the water continuously moves toward the free surface, where it evaporates, which induces a constant drying rate. Thus, we can also write $j = \rho_0 D_0 (1 - n_\infty) / \delta$. Finally, the characteristic thickness of the boundary layer under such conditions can be deduced from the equality of the two vapor flux expressions above, leading to

$$\delta = \frac{\rho_0 D_0 A}{m_{\text{dry}}} \left(\frac{\partial s}{\partial t} \right).$$

Note that in this expression the variations of D_0 with temperature (typically $D_0 T \propto n^{1.8}$) can be taken into account. However, in the range of temperatures covered in this study, they induce a maximum variation of δ by a factor 1.17, which has a negligible impact on the diffusion characteristics under our relatively high air flux intensity (i.e., δ on the order of 1 mm).

APPENDIX B: NMR RELAXOMETRY DATA FOR OAK

Typical NMR relaxometry data for oak, i.e., the PDF evolution over time during a drying test with an oil-filled sample, are presented Fig. 10.

APPENDIX C: SORPTION CURVES

Sorption data for the different materials are shown in Fig. 11. In all cases, the desorption curves are shown,

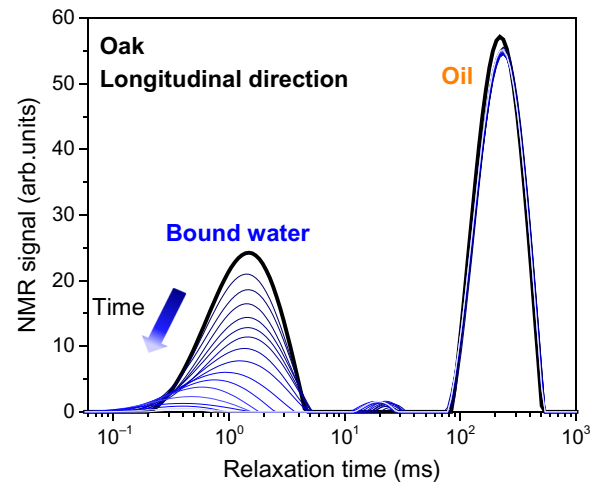


FIG. 10. Probability density function of the transverse relaxation time of bound water and oil in oak during drying at ambient temperature. The thick black line corresponds to the initial state. The distributions (from top to bottom) are shown at different successive times: 0, 0.25, 0.9, 2.2, 3.5, 4.9, 6.8, 9.4, 12.5, 18, 24.5, 30.9, 39.4, 51, 61.4, 75, and 88 h.

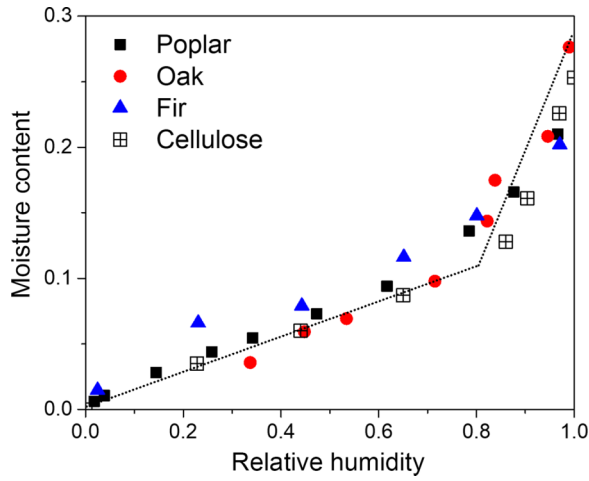


FIG. 11. Sorption data used in this study. Cellulose fiber data are from Ref. [31], oak desorption data are our own data, poplar data are from Ref. [77] (desorption curve for unmodified wood, rescaled with our maximum moisture content for bound water), and fir sorption data are from Ref. [78].

except for fir. For cellulose, long times at each humidity level allowed us to obtain similar sorption and desorption curves [76]. For oak and cellulose, the data align along a slope that goes through zero moisture content for relative humidity tending to 0%, and they can be represented by a straight line up to relative humidity of 80%. For relative humidity greater than 80%, the data are well represented by a slope of 1. Although the shapes of the sorption curves for fir and poplar are somewhat more complex, the slope of the experimental curve can still be well represented by a slope of 0.13 over most of the range of relative humidity between 0% and 80%, and approximately by a slope of 1 beyond this range.

The sorption and desorption curves change when the temperature varies, but in a rather limited way in the range from 10 to 50 °C (see the data in Refs. [4,79]). Finally, the representation of the slope of the desorption curve by the model described above seems to be a good approximation.

APPENDIX D: NUMERICAL SIMULATION

To solve the one-dimensional diffusion equation, an explicit finite-difference method is implemented. Specifically, the forward-time, central-space (FTCS) scheme was applied, with the use of a forward difference for the time derivative and a second-order central difference for the spatial derivative. The stability of this explicit FTCS scheme is governed by the Courant-Friedrichs-Lewy condition, i.e., $\alpha = D\Delta t/\Delta x^2 \leq 0.5$, where D is the diffusion coefficient, Δt is the time step, and Δx is the spatial step. In our cases, the values chosen for Δt , Δx , and D ensure numerical stability. The initial condition along the whole wood sample is assumed as fully saturated, i.e., $S = 1$. The left

boundary (the bottom surface of wood, i.e., $x = 0$) is considered impermeable, and is set as the no-flux boundary, $\partial S/\partial x = 0$, and the right boundary (the wood-air interface, $x = H$) is set as a Fourier-type boundary [Eq. (2)]. The relative humidity distribution $n(x, t)$ along the thickness of the boundary layer δ for vapor diffusion is firstly computed, and afterwards, at the exchange interface of vapor with wood ($x = H$), this relative humidity is converted to the distribution of moisture content $s(x, t)$ at each time step, on the basis of the desorption isotherm curve $s = f(n)$.

APPENDIX E: IMPACT OF THE PRESENCE OF VOID INCLUSIONS IN THE SOLID MATRIX

Although the void inclusions are, in principle, enclosed by the surrounding solid matrix or the oil, they can participate in the water transport during our drying tests. Indeed, they contain air and vapor, due to the constant exchange between vapor and bound water. Following continuum homogenization, the effective diffusivity D of a heterogeneous medium is related to the diffusivities of its constituting phases depending on its microstructure. For a medium made of a matrix of diffusivity D_b (bound water) containing disconnected inclusions of diffusivity D_v (vapor), a reasonable homogenization model is the Maxwell-Eucken estimation [80]:

$$D = D_b \left(\frac{2D_b + D_v - 2(D_b - D_v) \times \Phi}{2D_b + D_v + (D_b - D_v) \times \Phi} \right),$$

in which Φ is the volume fraction of inclusions. This estimate is not applicable directly to the transport diffusion coefficient, as the driving force (gradient of density $\nabla \rho$) is not the same for the matrix and the inclusions (bound water density is very different from vapor density). An appropriate common driving force is the gradient

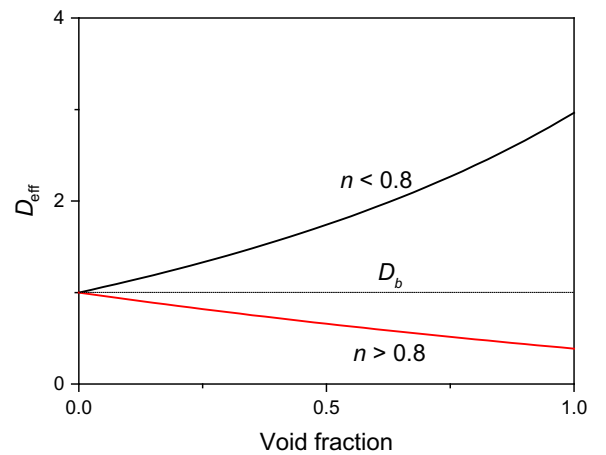


FIG. 12. Typical impact of the presence of voids on the diffusivity of the matrix for a temperature of 20 °C and a diffusion coefficient in the solid phase of 10^{-9} m²/s.

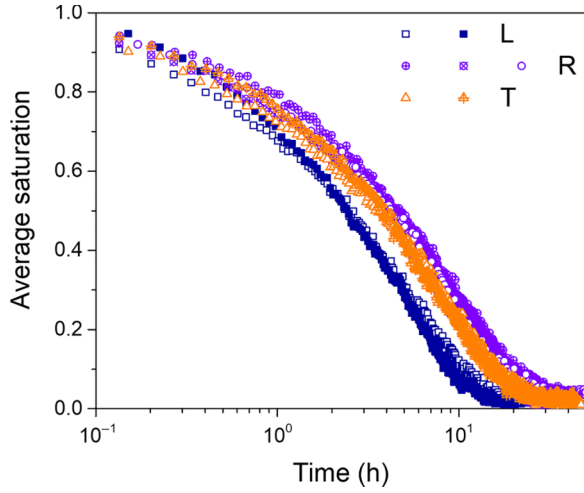


FIG. 13. Saturation over time during the drying of oil-filled poplar samples along different surfaces, resulting in transport in the main directions of wood at 28 °C. For each direction, the results of several tests conducted under the same conditions with different samples are presented. L, longitudinal direction; R, radial direction; T, tangential direction.

of humidity ∇n , and the corresponding diffusivity D_n is related to the transport diffusivity according to $D_n \nabla n = D_T \nabla \rho \Rightarrow D_n = D_T (\partial \rho / \partial n)_T$. The partial derivative for the vapor is the saturation density, $(\partial \rho / \partial n)_T = \rho_{\text{sat}}(T)$; for the matrix, it is given by the slope of the adsorption isotherm, $\alpha = (\partial \rho / \partial n)_T$. The water density may be approximated by $\rho = s \rho_s$, in which $\rho_s = 1500 \text{ kg/m}^3$ is the density of the solid phase (essentially cellulosic). Since the adsorption isotherm is roughly piecewise linear (see Fig. 11), we can approximate it by two straight lines, i.e., $s = 0.13n$ for

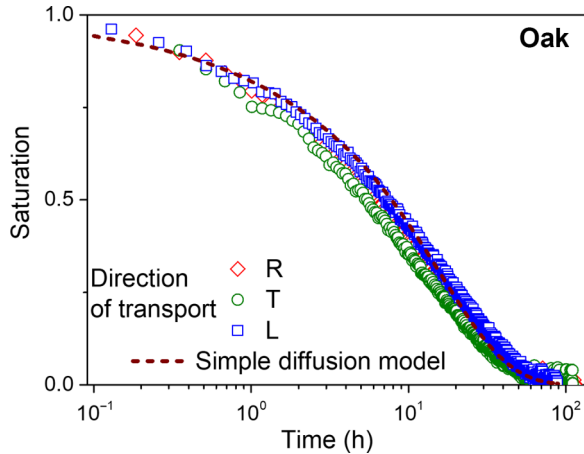


FIG. 14. Saturation over time during the drying of oil-filled oak samples along different surfaces, leading to transport in the main directions of wood at 28 °C. The dotted line corresponds to the simple diffusion model fitted to oak data (longitudinal direction) with diffusion coefficient $D = 0.75 \times 10^{-9} \text{ m}^2/\text{s}$. L, longitudinal; R, radial; T, tangential.

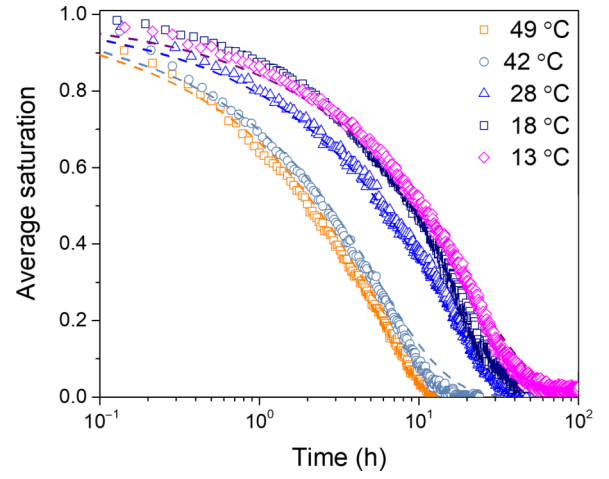


FIG. 15. Saturation vs time curves during the drying of cellulose fiber composites at different temperatures. The dotted lines correspond to model fitting with a constant diffusion coefficient. The values of the resulting diffusion coefficient are presented in Fig. 9(b).

$n < 0.8$ and $s = n - 0.74$ for $n > 0.8$, as proposed for cellulose [31], so α is represented by two constant values in these two ranges of n . These values remain fairly constant over the temperature range in this study (see Fig. 15). It is important to note that in this description we ignored porosity changes resulting from bound water absorption. Actually, it was observed that water absorption induces a global volume change of a poplar sample larger than the volume change strictly associated with the absorbed water volume (by a factor of 1/0.7; see Ref. [22]). Considering the porosity of poplar [about 67%, as deduced from our data (see Sec. II A)], this indicates that the pore size also increases when the solid phase swells, and finally the porosity only decreases to 62.5% when the medium is saturated with bound water. Since the mass of water vapor is negligible in the effective medium, $(d\rho/dn)_T^{\text{eff}} \approx (d\rho/dn)_T^b = \alpha$. Therefore, the effective transport diffusion coefficient is given by

$$D = D_b \left(\frac{2\alpha D_b + \rho_{\text{sat}} D_v + 2(\rho_{\text{sat}} D_v - \alpha D_b) \times \Phi}{2\alpha D_b + \rho_{\text{sat}} D_v - (\rho_{\text{sat}} D_v - \alpha D_b) \times \Phi} \right).$$

On the basis of this relation, one can estimate the transport diffusivity D_b of bound water in the matrix using the known vapor diffusivity as a function of temperature [81]: $D_v(T) = D_{v,\text{ref}}(T/T_0)^{1.81}$, where $D_{v,\text{ref}} = 2.178 \times 10^{-5} \text{ m}^2/\text{s}$ and $T_0 = 273.15 \text{ K}$.

APPENDIX F: IMPACT OF WOOD DIRECTION AND REPRODUCIBILITY

Saturation versus time data from drying tests under similar conditions on poplar samples along different directions are presented in Fig. 13. Data corresponding to several

tests with different samples under the same conditions are rather well superimposed, say, within about 10%, which illustrates the good reproducibility of the data. Note that here for poplar, in contrast with our findings for oak and fir, there exists a noticeable difference between the data in the longitudinal direction and the data in the other two directions. Specifically, the diffusion coefficient is about 1.5 times larger in the longitudinal direction. Data for oak samples in the different directions are presented in Fig. 14.

APPENDIX G: DIFFUSION DATA FOR CELLULOSE

The saturation versus time curves for cellulose samples at different temperatures are presented in Fig. 15.

-
- [1] H. O'Neill, S. V. Pingali, L. Petridis, J. He, E. Mamontov, L. Hong, V. Urban, B. Evans, P. Langan, J. C. Smith, and B. Daviso, Dynamics of water bound to crystalline cellulose, *Sci. Rep.* **7**, 11840 (2017).
 - [2] A. Paajanen, A. Zitting, L. Rautkari, J. A. Ketoja, and P. A. Penttilä, Nanoscale mechanism of moisture-induced swelling in wood microfibril bundles, *Nano Lett.* **22**, 5143 (2022).
 - [3] A. Zitting, A. Paajanen, L. Rautkari, and P. A. Penttilä, Deswelling of microfibril bundles in drying wood studied by small-angle neutron scattering and molecular dynamics, *Cellulose* **28**, 10765 (2021).
 - [4] E. E. Thybring, M. Fredriksson, S. L. Zelinka, and S. V. Glass, Water in wood: A review of current understanding and knowledge gaps, *Forests* **13**, 2051 (2022).
 - [5] K. Kulasinski, R. Guyer, D. Derome, and J. Carmeliet, Water adsorption in wood microfibril-hemicellulose system: Role of the crystalline-amorphous interface, *Biomacromolecules* **16**, 2972 (2015).
 - [6] W. T. Simpson, Drying and control of moisture content and dimensional changes, *Wood Handbook: Wood as an Engineering Material* (USDA Forest Service, Forest Products Laboratory, Madison, WI, 1999), p. 12.1. General Technical Report FPL; GTR-113.
 - [7] J. E. Jakes, C. G. Hunt, S. L. Zelinka, P. N. Ciesielski, and N. Z. Plaza, Effects of moisture on diffusion in unmodified wood cell walls: A phenomenological polymer science approach, *Forests* **10**, 1084 (2019).
 - [8] C. A. Hill, A. Norton, and G. Newman, The water vapor sorption behavior of natural fibers, *J. Appl. Polym. Sci.* **112**, 1524 (2009).
 - [9] S. Hameury, Moisture buffering capacity of heavy timber structures directly exposed to an indoor climate: A numerical study, *Build. Environ.* **40**, 1400 (2005).
 - [10] O. F. Osanyintola and C. J. Simonson, Moisture buffering capacity of hygroscopic building materials: Experimental facilities and energy impact, *Energy Build.* **38**, 1270 (2006).
 - [11] Y. Li, P. Fazio, and J. Rao, An investigation of moisture buffering performance of wood paneling at room level and its buffering effect on a test room, *Build. Environ.* **47**, 205 (2012).
 - [12] D. Kraniotis and K. Nore, Latent heat phenomena in buildings and potential integration into energy balance, *Proc. Environ. Sci.* **38**, 364 (2017).
 - [13] S. Avramidis, Bound water migration in wood, in *Advances in the drying of wood. COST E15* (2018).
 - [14] D. Elustondo, N. Matan, T. Langrish, and S. Pang, Advances in wood drying research and development, *Dry. Technol.* **41**, 890 (2023).
 - [15] S. Park, R. A. Venditti, H. Jameel, and J. J. Pawlak, Hard to remove water in cellulose fibers characterized by high resolution thermogravimetric analysis-methods development, *Cellulose* **13**, 23 (2006).
 - [16] A. K. Ghosh, in *Evaporation, Condensation and Heat Transfer* (IntechOpen, London, 2011).
 - [17] E. Bosco, R. Peerlings, B. Lomans, C. van der Sman, and M. Geers, On the role of moisture in triggering out-of-plane displacement in paper: From the network level to the macroscopic scale, *Int. J. Solids. Struct.* **154**, 66 (2018).
 - [18] P. A. M. Zapata, M. Fransen, J. ten Thije Boonkkamp, and L. Saes, Coupled heat and moisture transport in paper with application to a warm print surface, *Appl. Math. Model.* **37**, 7273 (2013).
 - [19] M.-L. Dano and J.-P. Bourque, Deformation behaviour of paper and board subjected to moisture diffusion, *Int. J. Solids Struct.* **46**, 1305 (2009).
 - [20] K. Sandberg and J.-G. Salin, Liquid water absorption in dried norway spruce timber measured with CT scanning and viewed as a percolation process, *Wood Sci. Technol.* **46**, 207 (2012).
 - [21] Ö. Gezici-Koç, S. J. Erich, H. P. Huinink, L. G. Van der Ven, and O. C. Adan, Bound and free water distribution in wood during water uptake and drying as measured by 1D magnetic resonance imaging, *Cellulose* **24**, 535 (2017).
 - [22] M. Zhou, S. Caré, D. Courtier-Murias, P. Faure, S. Rodts, and P. Coussot, Magnetic resonance imaging evidences of the impact of water sorption on hardwood capillary imbibition dynamics, *Wood Sci. Technol.* **52**, 929 (2018).
 - [23] M. Zhou, S. Caré, A. King, D. Courtier-Murias, S. Rodts, G. Gerber, P. Aïmedieu, M. Bonnet, M. Bornert, and P. Coussot, Wetted enhanced by water adsorption in hygroscopic plantlike materials, *Phys. Rev. Res.* **1**, 033190 (2019).
 - [24] L. Yan, E. Julien, B. Maillet, R. Sidi-Boulénouar, and P. Coussot, Water penetration in the microstructure of hardwood revealed by NMR relaxometry, *Wood Sci. Technol.* **59**, 29 (2025).
 - [25] X. Li, X. Wang, and M. Zhang, An investigation of the drying rate of water in wood at different relative humidities studied by time domain nuclear magnetic resonance, *BioResources* **12**, 2991 (2017).
 - [26] Z. Wang, X.-M. Wang, and Z.-J. Chen, Water states and migration in Xinjiang poplar and Mongolian scotch pine monitored by TD-NMR during drying, *Holzforschung* **72**, 113 (2018).
 - [27] H. Penvern, M. Zhou, B. Maillet, D. Courtier-Murias, M. Scheel, J. Perrin, T. Weitkamp, S. Bardet, S. Caré, and P. Coussot, How bound water regulates wood drying, *Phys. Rev. Appl.* **14**, 054051 (2020).
 - [28] M. Cocusse, M. Rosales, B. Maillet, R. Sidi-Boulénouar, E. Julien, S. Caré, and P. Coussot, Two-step diffusion in

- cellular hygroscopic (vascular plant-like) materials, *Sci. Adv.* **8**, eabm7830 (2022).
- [29] Y. Zou, B. Maillet, L. Brochard, and P. Coussot, Fast transport diffusion of bound water in cellulose fiber network, *Cellulose* **30**, 7463 (2023).
- [30] *Standard Test Methods for Water Vapor Transmission of Materials—ASTM E96-95* (ASTM, West Conshohocken, PA, USA, 2004).
- [31] Y. Zou, B. Maillet, L. Brochard, and P. Coussot, Unveiling moisture transport mechanisms in cellulosic materials: Vapor vs. bound water, *PNAS Nexus* **3**, pgad450 (2024).
- [32] K. Kelsey, The sorption of water vapor by wood., *Aust. J. Appl. Sci.* **8**, 42 (1957).
- [33] S. V. Dvinskikh, M. Henriksson, L. A. Berglund, and I. Furó, A multinuclear magnetic resonance imaging (MRI) study of wood with adsorbed water: Estimating bound water concentration and local wood density, *Holzforschung* **65**, 103 (2011).
- [34] A. J. Stamm, Movement of fluids in wood—Part I: Flow of fluids in wood, *Wood Sci. Technol.* **1**, 122 (1967).
- [35] S. Avramidis and J. Siau, An investigation of the external and internal resistance to moisture diffusion in wood, *Wood Sci. Technol.* **21**, 249 (1987).
- [36] B. Ramarao, A. Massoquete, S. Lavrykov, and S. Ramaswamy, Moisture diffusion inside paper materials in the hygroscopic range and characteristics of diffusivity parameters, *Dry. Technol.* **21**, 2007 (2003).
- [37] H. Radhakrishnan, S. Chatterjee, and B. Ramarao, Steady-state moisture transport in a bleached kraft paperboard stack, *J. Pulp Paper Sci.* **26**, 140 (2000).
- [38] A. Mackay, K. Whittall, J. Adler, D. Li, D. Paty, and D. Graeb, In vivo visualization of myelin water in brain by magnetic resonance, *Magn. Reson. Med.* **31**, 673 (1994).
- [39] P. Coussot, Progress in rheology and hydrodynamics allowed by NMR or MRI techniques, *Exp. Fluids* **61**, 1 (2020).
- [40] G. Almeida, S. Gagné, and R. E. Hernández, A nmr study of water distribution in hardwoods at several equilibrium moisture contents, *Wood Sci. Technol.* **41**, 293 (2007).
- [41] V. Stagno, F. Egizi, F. Corticelli, V. Morandi, F. Valle, G. Costantini, S. Longo, and S. Capuani, Microstructural features assessment of different waterlogged wood species by NMR diffusion validated with complementary techniques, *Magn. Reson. Imaging* **83**, 139 (2021).
- [42] A. Haase, Snapshot FLASH MRI applications to T1, T2, and chemical-shift imaging, *Magn. Reson. Med.* **13**, 77 (1990).
- [43] S. Emid and J. Creighton, High resolution NMR imaging in solids, *Physica B+ C* **128**, 81 (1985).
- [44] B. Maillet, G. Dittich, P. Huber, and P. Coussot, Diffusion-like drying of a nanoporous solid as revealed by magnetic resonance imaging, *Phys. Rev. Appl.* **18**, 054027 (2022).
- [45] Y. Zou, L. Yan, B. Maillet, R. Sidi-Boulouar, L. Brochard, and P. Coussot, Critical role of boundary conditions in sorption kinetics measurements, *Langmuir* **39**, 18866 (2023).
- [46] H. Y. Carr and E. M. Purcell, Effects of diffusion on free precession in nuclear magnetic resonance experiments, *Phys. Rev.* **94**, 630 (1954).
- [47] S. Meiboom and D. Gill, Modified spin-echo method for measuring nuclear relaxation times, *Rev. Sci. Instrum.* **29**, 688 (1958).
- [48] S. W. Provencher, A constrained regularization method for inverting data represented by linear algebraic or integral equations, *Comput. Phys. Commun.* **27**, 213 (1982).
- [49] K. P. Whittall and A. L. MacKay, Quantitative interpretation of NMR relaxation data, *J. Magn. Reson.* (1969) **84**, 134 (1989).
- [50] B. Maillet, R. Sidi-Boulouar, and P. Coussot, Dynamic NMR relaxometry as a simple tool for measuring liquid transfers and characterizing surface and structure evolution in porous media, *Langmuir* **38**, 15009 (2022).
- [51] K. Brownstein and C. Tarr, Spin-lattice relaxation in a system governed by diffusion, *J. Magn. Reson.* (1969) **26**, 17 (1977).
- [52] J. Crank, *The Mathematics of Diffusion* (Oxford University Press, Oxford, 1975), p. 21.
- [53] W. Simpson and J. Liu, Dependence of the water vapor diffusion coefficient of aspen (*Populus spec.*) on moisture content, *Wood Sci. Technol.* **26**, 9 (1991).
- [54] A. J. Stamm, Bound-water diffusion into wood in the fibre direction, *For. Prod. J.* **9**, 27 (1959).
- [55] A. Murr, Water vapour sorption and moisture transport in and across fibre direction of wood, *Cellulose* **29**, 4135 (2022).
- [56] D. Topgaard and O. Söderman, Diffusion of water absorbed in cellulose fibers studied with ¹H-NMR, *Langmuir* **17**, 2694 (2001).
- [57] K. Kulasinski, S. Ketten, S. V. Churakov, R. Guyer, J. Carmeliet, and D. Derome, Molecular mechanism of moisture-induced transition in amorphous cellulose, *ACS Macro Lett.* **3**, 1037 (2014).
- [58] A. Sánchez-Ferrer, M. Engelhardt, and K. Richter, Anisotropic wood–water interactions determined by gravimetric vapor sorption experiments, *Cellulose* **30**, 3869 (2023).
- [59] K. Kulasinski, S. Ketten, S. V. Churakov, D. Derome, and J. Carmeliet, A comparative molecular dynamics study of crystalline, paracrystalline and amorphous states of cellulose, *Cellulose* **21**, 1103 (2014).
- [60] C. Skaar, *Wood-Water Relations* (Springer Berlin Heidelberg, Berlin, Heidelberg, 1998).
- [61] A. J. Stamm, Diffusion of water into uncoated Cellophane. I. From rates of water vapor adsorption, and liquid water absorption, *J. Phys. Chem.* **60**, 76 (1956).
- [62] E. Choong, Diffusion coefficients of softwoods by steady-state and theoretical methods, *For. Prod. J.* **15**, 21 (1965).
- [63] G. Bramhall, Diffusion and the drying of wood, *Wood Sci. Technol.* **29**, 209 (1995).
- [64] M. Holz, S. R. Heil, and A. Sacco, Temperature-dependent self-diffusion coefficients of water and six selected molecular liquids for calibration in accurate ¹H NMR PFG measurements, *Phys. Chem. Chem. Phys.* **2**, 4740 (2000).
- [65] W. D. Callister Jr and D. G. Rethwisch, *Materials Science and Engineering: An Introduction* (John Wiley & Sons, Hoboken, 2020).
- [66] S. Glasstone, K. Laidler, and H. Eyring, *The Theory of Rate Processes* (McGraw-Hill Book Co, New York, 1941), p. 477.

- [67] W. Kellouai, J.-L. Barrat, P. Judeinstein, M. Plazenet, and B. Coasne, On De Gennes narrowing of fluids confined at the molecular scale in nanoporous materials, *J. Chem. Phys.* **160**, 024113 (2024).
- [68] C. Zhang, A. Shomali, B. Coasne, D. Derome, and J. Carmeliet, Sorption–deformation–percolation model for diffusion in nanoporous media, *ACS Nano* **17**, 4507 (2023).
- [69] K. Falk, B. Coasne, R. Pellenq, F.-J. Ulm, and L. Bocquet, Subcontinuum mass transport of condensed hydrocarbons in nanoporous media, *Nat. Commun.* **6**, 6949 (2015).
- [70] T.-Q. Li, U. Henriksson, T. Klason, and L. Ödberg, Water diffusion in wood pulp cellulose fibers studied by means of the pulsed gradient spin-echo method, *J. Colloid Interface Sci.* **154**, 305 (1992).
- [71] C. Araujo, A. MacKay, K. Whittall, and J. Hailey, A diffusion model for spin-spin relaxation of compartmentalized water in wood, *J. Magn. Reson. Ser. B* **101**, 248 (1993).
- [72] E. Perkins and W. Batchelor, Water interaction in paper cellulose fibres as investigated by NMR pulsed field gradient, *Carbohydr. Polym.* **87**, 361 (2012).
- [73] T. Maloney, J. Phiri, A. Zitting, A. Paajanen, P. Penttilä, and S. Ceccherini, Deaggregation of cellulose microfibrils and its effect on bound water, *Carbohydr. Polym.* **319**, 121166 (2023).
- [74] J.-L. Barrat and J.-P. Hansen, *Basic Concepts for Simple and Complex Liquids* (Cambridge University Press, Cambridge, 2003).
- [75] T. L. Bergman, A. S. Lavine, F. P. Incropera, and D. P. Dewitt, *Fundamentals of Heat and Mass Transfer* (John Wiley & Sons, Hoboken, 2011).
- [76] X. Ma, B. Maillat, L. Brochard, O. Pitois, R. Sidi-Boulénouar, and P. Coussot, Vapor-sorption coupled diffusion in cellulose fiber pile revealed by magnetic resonance imaging, *Phys. Rev. Appl.* **17**, 024048 (2022).
- [77] W. Olek, J. Majka, and Ł. Czajkowski, Sorption isotherms of thermally modified wood, *Holzforschung* **67**, 183 (2013).
- [78] M. Bonnet, D. Courtier-Murias, P. Faure, S. Rodts, and S. Care, Nmr determination of sorption isotherms in earlywood and latewood of Douglas fir. Identification of bound water components related to their local environment, *Holzforschung* **71**, 481 (2017).
- [79] J. F. Siau, in *Transport Processes in Wood* (Springer-Verlag, Berlin, 1984), p. 1.
- [80] J. K. Carson, S. J. Lovatt, D. J. Tanner, and A. C. Cleland, Thermal conductivity bounds for isotropic, porous materials, *Int. J. Heat Mass Transfer* **48**, 2150 (2005).
- [81] W. Massman, A review of the molecular diffusivities of H₂O, CO₂, CH₄, CO, O₃, SO₂, NH₃, N₂O, NO, and NO₂ in air, O₂ and N₂ near STP, *Atmos. Environ.* **32**, 1111 (1998).