THE DETERMINATION OF THE CELL SIZE IN WOOD BY NUCLEAR MAGNETIC RESONANCE DIFFUSION TECHNIQUES

Wei Wycoff

NMR Spectroscopist
Department of Chemistry

Stephen Pickup

Research Assistant Professor
Department of Radiology

Bruce Cutter†

Associate Professor
Department of Forestry
School of Natural Resources

William Miller

Professor
Department of Nuclear Engineering

and

Tuck C. Wong

Professor
Department of Chemistry
University of Missouri
Columbia, MO 65211

ABSTRACT

Two nuclear magnetic resonance (NMR) pulsed field gradient diffusion approaches have been applied to the measurement of the magnitude and the distribution of the tangential dimension of cells in a number of wood samples. The results thus obtained were compared with the results from microscopy. The results from these two approaches agree with each other and they also give excellent agreement with the microscopy results. The results of this work demonstrate that NMR diffusion is an accurate and convenient method for the measurement of cell sizes in wood and in similar porous systems.

Keywords: NMR, cell size, diffusion, wood.

INTRODUCTION

In gymnosperms (frequently referred to as softwoods), wood cell size is directly related to utilization factors, particularly mechanical properties and machining characteristics. One indicator of cell size is the tangential diameter of the longitudinal tracheid, by far and away the most common cell type found in temperate zone gymnosperms. The longitudinal tracheid functions as both the supporting element for the tree as well as the avenue of conduction for water and nutrients involved in photosynthesis. Cells produced by the same cambial initial will change vary little in tangential di-

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† Member of SWST.

mension from year to year but will vary from beginning to end of the growth season in their radial dimensions.

Nuclear magnetic resonance diffusion methods have been shown to be well suited to the study of fluids in heterogeneous media. Direct measurements of the translational diffusion using pulsed-field gradient spin echo (PFGSE) and similar techniques can reveal barriers to diffusion and thus provide a way to measure boundary dimensions and geometry (McCall et al. 1963; Stejskal and Tanner 1965; Callaghan 1984; Stilbs 1987).

In this work, NMR diffusion techniques have been applied to measure the diffusion of water in wood, and subsequently, to measure the average tangential dimensions and the distribution of the tangential dimension of cells in wood. The results have been compared with similar measurements of the same samples by microscopy.

Longitudinal tracheids comprise over 90% of the wood volume in softwoods. These cells are typically described as needle-shaped, and the interior cavity, the lumen, reflects the exterior shape as well. The four commercial wood species investigated provided a wide range of cell sizes. Eastern red cedar (*Juniperus virginiana* L.) has the smallest tracheids among commercial North American softwood in both tracheid tangential diameter and length. Published cell dimensions for red cedar are 25 μm in tangential diameter with an average cell length of about 2 mm. Redwood (*Sequoia sempervirens* L.), on the other hand, has the largest average diameter (50–65 μm) and length (5 to 8 mm). Eastern white pine (*Pinus strobus* L.) and sugar pine (*Pinus lambertiana* Dougl.) are relatively intermediate in these dimensions with tangential diameters of 25 to 35 μm and 40 to 50 μm, respectively, and cell lengths of 3 to 4 mm and 5 mm, respectively (Panshin and de Zeeuw 1980). Their longitudinal dimensions are long compared with the diffusion length of water in a typical PFG diffusion experiment (with a maximum diffusion time, Δ, of ≤ 1s). The cell barriers in the longitudinal direction, therefore,

will not appear as barriers to diffusion in the PFGSE experiment. Therefore, in this work, only the tangential dimensions of cells in wood were evaluated.

THEORY

Estimation of cell size based on apparent diffusion coefficient vs. diffusion time

Calculation of apparent diffusion coefficient D' for a given diffusion time Δ.—The echo intensity $I(\Delta, \delta, g)$ obtained in the PFGSE experiment is related to the gradient amplitude g by the following equation (Stejskal and Tanner 1965):

$$I(\Delta, \delta, g) = I(\Delta)\exp\{-\gamma^2 g^2 \delta^2 D(\Delta - \delta/3)\} \quad (1)$$

where $I(\Delta)$ is the echo intensity in the absence of gradient, γ is the magnetogyric ratio of protons, δ is the gradient pulse duration, D is the diffusion constant, and Δ is the diffusion time. In the absence of barriers to diffusion, D thus obtained should be independent of Δ. Equation (1) may also be applied to systems undergoing restricted diffusion (Lauffer 1974). In that case, the diffusion coefficient D in Eq. (1) is replaced by an effective or apparent diffusion coefficient D'.

For wood samples with high water content, the water signal observed by NMR is primarily due to the "free" water which is not associated with the cell walls. A small portion of the signal is contributed by water molecules that are "bound" to the cell walls by, for example, strong hydrogen bonding (Sharp et al. 1978). The diffusion of the water bound to cell walls is so slow relative to the diffusion time, Δ, that its signal appears constant in a PFGSE experiment. A constant term, A, is added to Eq. (1) to account for the contribution to the water signal from bound water:

$$I(\Delta, \delta, g) = A + I(\Delta)\exp\{-\gamma^2 g^2 \delta^2 D'(\Delta - \delta/3)\} \quad (2)$$

Since all parameters except g in the second term of Eq. (2) are constant at a given Δ, Eq. (2) can be rewritten as

$$I(\Delta, \delta, g) = A + B\exp\{Cg^2\} \quad (3)$$

where $B = I(\Delta)$ and $C = -(\gamma\delta)^2 D'(\Delta - \delta/3)$. A, B, and C can be obtained by fitting the data of $I(\Delta, \delta, g)$ vs. g^2. D' can then be calculated from C by Eq. (4):

$$D' = C/[-(\gamma\delta)^2(\Delta - \delta/3)] \qquad (4)$$

Evaluation of cell size.—From Eq. (1), we can obtain

$$D' = -\ln E/[K^2(\Delta - \delta/3)] \qquad (5)$$

where the attenuation of the spin echo $E = I(\Delta, \delta, g)/I(\Delta)$ and $K = \gamma g\delta$. It has been shown (Tanner and Stejskal 1968) that for diffusion between perfectly reflective parallel planes, E reaches an asymptotic value E_∞ as Δ increases without bond:

$$\ln E^\circ_\infty \equiv \lim_{K\to 0} \ln E_\infty \sim -(K2a)^2/12 \qquad (6)$$

where $2a$ is the distance between the barriers. Substitution of this result into Eq. (5) yields

$$D'_\infty = -\ln E^\circ_\infty/[K^2(\Delta_\infty - \delta/3)]$$

$$= (2a)^2/[12(\Delta_\infty - \delta/3)] \qquad (7)$$

The experimental condition is such that $\Delta_\infty \gg \delta/3$. The $\delta/3$ term can therefore be omitted to give

$$D'_\infty = (2a)^2/(12\Delta_\infty) \qquad (8)$$

Equation (8) can be used to estimate $2a$ from D'_∞ and Δ_∞, which are obtained by extrapolation of a plot of D' vs. Δ.

Estimation of cell size based on echo attenuation $E(q, \Delta, a)$ vs. the reciprocal space vector q

An alternative approach to the evaluation of restricted diffusion data is to incorporate the geometry directly into the echo attenuation equation. In order to do so, it is necessary to assume that the gradient pulses are very short relative to the diffusion time. We must also make assumptions about the geometry of the system. The microscopy images showed that the cells in wood samples have rectangular cross sections (Fig. 1B) and are best described by the parallel planes geometry. For some
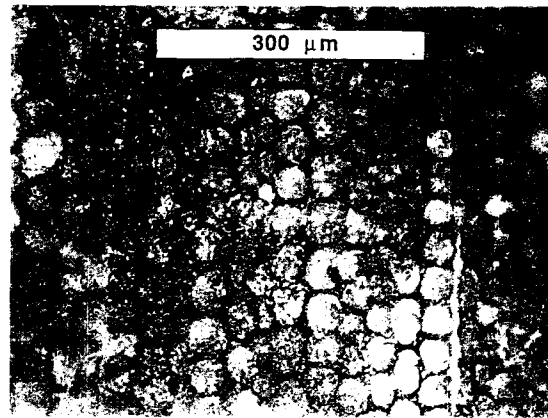
A
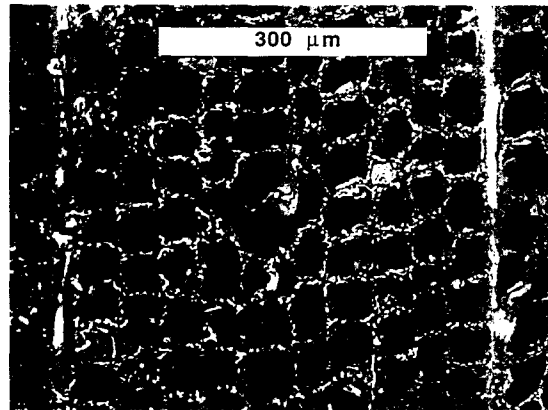
B

Fig. 1.   Microscopy pictures of eastern white pine sample 1 (A) and redwood sample 1 (B) taken with magnification of 152×.

samples, the shape is close to being cylindrical, for example for eastern white pine as shown in Fig. 1A. In the current work, we have assumed the parallel planes geometry in our treatment except for the eastern red cedar sample, for which both the parallel planes and cylindrical geometries were used. Under the short gradient pulse assumption, the echo attenuation in the presence of obstructions con-

sisting of parallel planes is given by (Callaghan 1995)

$$E(q, \Delta, a)$$

$$= 2 \sum_{n=0}^{\infty} \exp\left\{-\frac{\xi_n^2 D\Delta}{a^2}\right\}$$

$$\cdot \left(\{[(2\pi qa)\sin(2\pi qa)\cos \xi_n - \xi_n\cos(2\pi qa)\sin \xi_n]^2\}\right.$$

$$\div \{(1 + \sin(2\xi_n)/2\xi_n)[(2\pi qa)^2 - \xi_n^2]^2\}\right)$$

$$+ 2 \sum_{m=0}^{\infty} \exp\left\{-\frac{\zeta_m^2 D\Delta}{a^2}\right\}$$

$$\cdot \left(\{[(2\pi qa)\cos(2\pi qa)\sin \zeta_m - \zeta_m\sin(2\pi qa)\cos \zeta_m]^2\}\right.$$

$$\div \{(1 - \sin(2\zeta_m)/2\zeta_m)$$

$$\left.\cdot [(2\pi qa)^2 - \zeta_m^2]^2\}\right) \qquad (9)$$

where $q = \gamma g\delta/2\pi$ and D is the self-diffusion coefficient in the absence of barriers. The parameters ξ and ζ are eigen values and are solutions to the equations

$$\xi_n\tan \xi_n = \frac{Ma}{D} \qquad \zeta_m\tan \zeta_m = -\frac{Ma}{D} \qquad (10)$$

where M is the rate of magnetization loss at the obstruction surface. This surface decay includes contributions from surface-enhanced relaxation as well as the permeability of the surface. The contribution of each term in the summation decreases with increasing order. It is therefore safe to truncate the series. In the present study, the series was truncated at $n_{max} = m_{max} = 10$. For a detailed description of the pertinent equations for the cylindrical geometry, please refer to the work of Callaghan (Callaghan 1995).

Preliminary attempts to fit our data to Eq. (9) did not yield satisfactory results (data not shown). This failure was attributed to the distribution of cell sizes present in our samples. This distribution of cell sizes was also indicated in the microscopy pictures. The data were therefore fit to a weighted distribution of the equation above as given by

$$E_{calc} = \sum_{i}^{N} w_i(a_i, \sigma a)E(q, \Delta, a_i) \qquad (11)$$

where the weights, w_i, were assumed to have a Gaussian distribution

$$w(a, \delta a) = \exp\left\{-\left(\frac{a}{\sigma a}\right)^2\right\} \qquad (12)$$

and σa is the width of the distribution. The distribution was sampled with 16 points over a range of ± 2 σa. Nonlinear optimization techniques were used to find the values of the parameters a, σa, and M which minimize the difference between experimental echo intensities and that predicted by Eq. (12) for a given value of Δ.

EXPERIMENTAL

Samples

Small sticks of wood were cut from blocks of each wood species with the grain parallel to the long axis, which measured about 2.5 cm. The largest diameter is about 5 mm. The sticks were saturated by submerging in water under vacuum (26–27 torr) for 24 h. The vacuum was alternated every 2 h with atmospheric pressure. The samples were considered saturated when no further air bubbles issued from the samples. They were then removed from the vacuum, and any excess water on the surface of the sample was blotted off with tissue paper. The samples were then inserted into 5-mm OD NMR sample tubes. Slight trimming to reduce the diameter of each stick was sometimes required in order to fit into the tubes. The tubes were capped and sealed with parafilm.

NMR Spectroscopy

All NMR experiments were performed at 25°C on a Bruker DRX500 spectrometer equipped with a triple-axis gradient system and with proton frequency of 500.13 MHz. The maximum gradient amplitude, which was calibrated by the known diffusion coefficient of water (Mills 1973), is 48.6 Gauss/cm (G/cm) for each of the transverse x and y axes

and 62.5 G/cm for the axial z axis. A Bruker 5-mm triple-axis inverse-detection broadband probe was used. The S/N of the proton signal from free water inside the sample was large enough to be detected with one scan. The line-width at half height was about 100 Hz. In order to set appropriate repetition time in the diffusion experiment, the longitudinal relaxation time, T_1, of the water signal from each sample was estimated by the inversion-recovery technique. The T_1 values ranged from 0.4 to 1.7 s. The diffusion measurements were performed using the Pulse-Field-Gradient STimulated Echo (PFG-STE, Tanner 1970) pulse sequence with gradient pulse duration δ of 2 ms. Four scans were acquired at each gradient amplitude using 2K points with a spectral window of 4650 Hz. A repetition delay of five times of the estimated T_1 was used for all the diffusion studies. Further experimental details are described in the following paragraphs.

Apparent diffusion coefficient D' vs. diffusion time Δ.—Since the grain of the wood is parallel to the magnetic field direction (z axis), in order to measure the tangential cell size, gradient must be applied along the x or y axis. In our study both x and y gradients (g_x, g_y) were applied simultaneously with equal amplitude ($g_x = g_y$). D' was measured at 21 Δ values ranging from 13 to 903 ms. For each Δ, 15 echo intensity values were obtained as a function of gradient strengths g^2 as in Eq. (3), which in this case should be expressed as $g_x^2 + g_y^2$. Only g_x values are given here and they are reported as the percentages of the maximum amplitude of 48.6 G/cm on the x axis. The minimum applied g_x was 3%, and it was incremented at intervals of 4% for Δ less than 183 ms, 3% for Δ between 183 and 363 ms, and 2% for Δ larger than 363 ms. The maximum applied g_x was 59%, 45%, and 31%, respectively, for the three stages of Δ. A complete set of data consisted of 315 FIDs and took 1 to 3 h of instrument time.

For the evaluation of diffusion in the longitudinal direction in the eastern white pine sample, the z gradient was applied and it var-

ied from 3–87% of the maximum gradient amplitude of 62.5 G/cm.

Echo-attenuation E(q, Δ, a) vs. q.—At a fixed Δ (603 ms), echo intensity was measured as a function of g_x alone varying from 3 to 95% with a 1% increment. The echo intensity was also obtained with $g_x = 0$ using the same PFG-STE pulse sequence in order to obtain the echo-attenuation $E(q, \Delta, a)$. A complete set of data consisted of 94 FIDs and took 20 min to 1 h of instrument time.

Microscopy

Tangential cell-size measurements were performed on the wood samples after they had been used for NMR measurements. A set of cross-section pictures were obtained from a Nikon Epiphot 200 microscope equipped with a video graphic printer at magnification scales of 152× and 380×. Pictures were taken while the samples were saturated with water. The sample's surface was fast-dried to avoid optical distortions created by the water, and to improve picture quality. From each picture, the edge-to-edge distance for a series of well-defined tangential cells was measured, and the average distance obtained. The average thickness of the cell walls was measured in the same fashion and then subtracted from the first average number. In Fig. 1, the pictures taken with 152× magnification on an eastern white pine and a redwood sample are shown.

DATA ANALYSIS

Cell size estimation from D' vs. Δ data

Apparent diffusion coefficient D'.—Each set of echo intensity $I(\Delta, \delta, g)$ vs. g^2 data consisting of 15 points was fitted to Eq. (3) using the T1/T2 SIMFIT routine provided by Bruker's XWIN-NMR software to obtain C. An example of the SIMFIT result is shown in Fig. 2. The apparent diffusion coefficient D' was calculated from C according to Eq. (4).

Finding D'_x and Δ_x.—The D' vs. Δ data were fitted to a single exponential curve using the routine:
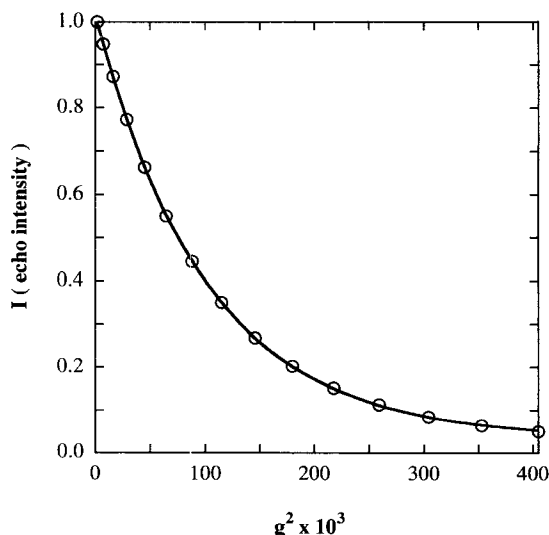
$$D' = A' + B'\exp\{-C'\Delta.\} \qquad (13)$$

FIG. 2. Redwood sample 2, echo intensity I vs. gradient strength g^2 ($g^2 = g_x^2 + g_y^2$, $g_x = g_y = 3$ to 45% of maximum gradient strength of 48.6 G/cm with 3% increment) at $\Delta = 303$ ms. Circles represent experimental data points and solid line represents SIMFIT result.
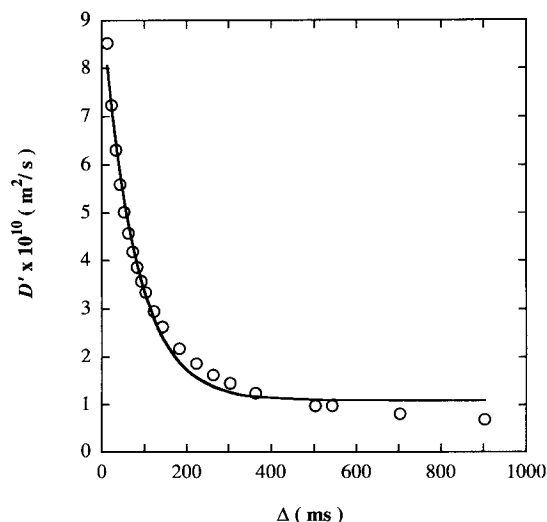

FIG. 3. The plot of D' vs. Δ for eastern white pine sample 1. Circles represent experimental data points and the solid line represents the result from a single exponential fit.

The parameters A', B', and C' were optimized. As shown in Fig. 3, D' reaches the near-asymptotic D'_∞ toward the longest Δ. We consider $D_\infty \cong A'$, and the Δ_∞ value was considered reached when the second term in Eq. (13) decreases to 0.1% of A'. After D'_∞ and Δ_∞ had been found, cell size $2a$ was calculated according to Eq. (8).

Cell size estimation from $E(q, \Delta, a)$ vs. q data

The simulated annealing (SA) method (Kirpatrick et al. 1983; Press and Teukolsky 1991; Rutenbar 1989) was used to minimize the sum of the squares of the difference between the experimental echo data and that calculated by Eq. (11). The implementation of the SA algorithm was similar to that previously described for the optimization of pulse envelopes (Geen et al. 1989). A geometrical annealing schedule was used as given by

$$T_n = \alpha T_n - 1 \tag{14}$$

where $\alpha = 0.98$. The parameters a, σa, and M were optimized in the calculation. A self-dif-

fusion coefficient of $D = 9.0 \times 10^{-9}$ m^2/s for water was used throughout the study. This value was based on an extrapolation of the apparent diffusion coefficient to zero Δ. The eigen values were calculated for each value of the cell-size parameter, a_i, using the Newton-Raphson method (Press et al. 1992). No attempt was made to optimize the computational efficiency of the optimizations. As such the computation times were substantial, requiring approximately 8 h of CPU time on an IBM RS6000 workstation for each data set. A typical set of $E(q, \Delta, a)$ vs. q data and the fitting are shown in Fig. 4.

RESULTS AND DISCUSSION

PFG-STE experiments on the eastern white pine, sample 2, using gradient pulses in the z direction yielded the apparent diffusion coefficients of 2.4×10^{-9} m^2/s at $\Delta = 13$ms and 2.0×10^{-9} m^2/s at the maximum Δ of 903 ms (Fig. 5). The D' value at the maximum Δ is still very close to the reported value of 2.2×10^{-9} m^2/s for bulk water (Simpson and Carr 1958). This indicates that water molecules do not encounter barriers to diffusion over the du-
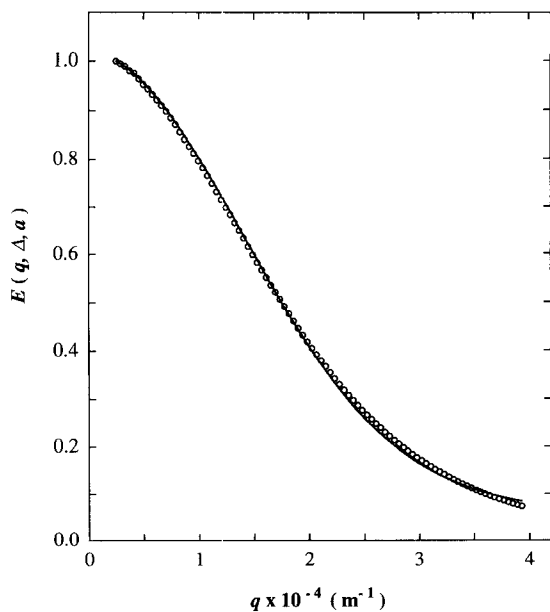
FIG. 4. The plot of $E(q, \Delta, a)$ vs. q for eastern red cedar sample 1. Circles represent experimental data points and solid line represents the SA result based on the parallel planes geometry. Both experimental and calculated data were normalized such that the first data point has a value of 1.

FIG. 5. The variation of the apparent diffusion coefficient of water, D', in eastern white pine as a function of the diffusion time, Δ, in the longitudinal (●) and in the tangential directions (○). The small decrease of D' in the longitudinal direction, and the closeness of its value to that of bulk water indicate that there is no barrier to diffusion in the longitudinal direction. The connecting lines are for illustration purpose only.

ration of the PFG-STE experiment in the longitudinal direction. The small decrease in D' at large Δ (about 10% at 903 ms) may indicate a certain degree of restriction, but not the impenetrable type as in the tangential direction. Knowing D' of 2.0×10^{-9} m²/s at the longest diffusion time of 903 ms, the limit of the measured distance is estimated to be 150 µm, much smaller than the longitudinal dimension of the cells. In contrast, experiments with gradient pulses in the transverse directions showed a variation of D' with Δ from 8.7×10^{-10} m²/s at $\Delta = 13$ ms to 8.5×10^{-11} m²/s at $\Delta = 903$ ms (Fig. 5) as indicated by Eq. (3). The substantially lower values of D' even at small Δ, and the large decrease in D' magnitude with increasing Δ (a factor of 10) indicate the effects of the barriers to diffusion.

The results on the measurement of the tangential diameter in the various samples studied by microscopy and the two NMR diffusion techniques are summarized in Table 1. The
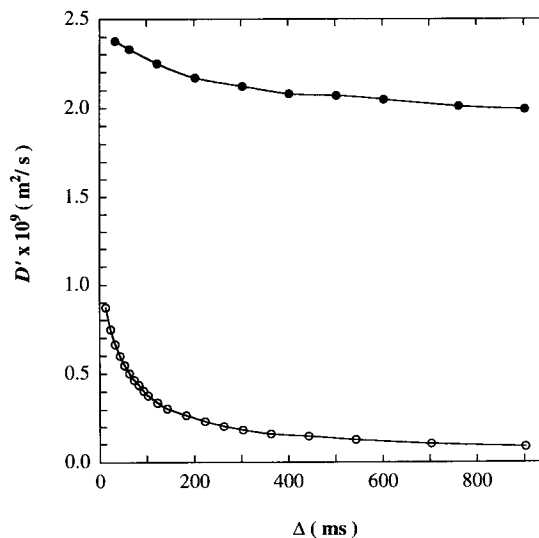
TABLE 1. Summary of tangential diameters (µm) obtained by different techniques.

Wood	[a]Microscopy	[b]D' vs. Δ	[c]E vs. q
sugar pine			
sample 1	42 ± 3	45 ± 3	
sample 2		47 ±3	48 ± 1 (14)
eastern red cedar			
sample 1		16 ± 2	25 ± 0 (12)[d]
			29 (13)[e]
sample 2	17 ± 1	17 ± 2	
eastern white pine			
sample 1	31 ± 1	30 ± 3	
sample 2		35 ± 3	34 ± 1 (13)
redwood			
sample 1	40 ± 1	43 ± 3	
sample 2		43 ± 3	42 ± 1 (17)

[a] Error estimated by results of several measurements directly from the pictures.

[b] Error estimated by the standard deviations of parameters A', B', and C' obtained as a result of fit to Eq. [13].

[c] Error estimated by variance in the results of duplicate runs of the simulated annealing. Number in bracket indicates the width of the tangential diameter distribution ($2 \times \sigma a$ in Eq. [12]).

[d] Duplicate runs showed practically no variance in the cell size.

[e] Result obtained from cylindrical geometry model. All other results in this column are based on the parallel planes model. No duplicate run was made for this calculation.

agreement is excellent among the results from these different methods. On the average, the values for the tangential diameter as measured by the NMR diffusion techniques are slightly higher than that obtained from microscopy. The differences, however, are within the respective experimental errors. The lone exception is the cell-size measurement for eastern red cedar where the cell size determined from the E vs. q approach (25 μm for parallel planes geometry and 29 μm for cylindrical geometry) is substantially higher than those from the measurements based on the other two methods (16–17 μm). The discrepancy was initially thought to be due to the use of the parallel planes model instead of the cylindrical model because the eastern red cedar sample actually has cylindrically shaped cells as revealed by the microscopy images (not shown). The subsequent results from the calculations based on both geometric models showed that the choice of the model for the cells does not significantly affect the results. Furthermore, among the four wood species studied, eastern white pine also had cylinder-shaped cells. However, unlike eastern red cedar, the results on the cell size in eastern white pine showed excellent agreement between different methods. Another plausible explanation for the apparent discrepancy on eastern red cedar is that the E vs. q measurements were made several months after the other two measurements. Cell size may have increased after such a prolonged period of saturation with water. This prolonged delay does not appear to cause discrepancies in other wood samples with larger cell size, however. In the E vs. q measurements and analysis, the distribution of tangential diameters ($2\sigma a$ in Eq. (12)) was also obtained. As defined in Eq. (12), σa is the width of the distribution. Since $2a$ represents the average tangential diameter, the distribution should be reported as $2\sigma a$. Typically, the distribution is between 25–30% of the cell size.

The excellent agreement between the results from microscopy and the NMR diffusion methods demonstrates that the NMR diffusion technique using the water molecules in wood

as a probe offers a convenient and accurate way of measuring the cell size in wood and in other systems of similar morphology. The E vs. q NMR experiment is more convenient to perform since it requires measurements at only one Δ value and takes less than an hour to collect data. Although the data analysis requires hours of CPU time, the result is more reliable. On the other hand, the D' vs. Δ experiment requires a series of Δ values and takes 1 to 3 h of data acquisition. Furthermore, the data analysis requires estimation of D'_{∞} and Δ_{∞} from the plot of D' vs. Δ. As shown in Fig. 3, D' vs. Δ is not a good fit to a single exponential function as defined in Eq. (13). In fact a perfect fit can be obtained if a second exponential term is added to Eq. (13) (data not shown) to account for a slower process, which might be diffusion of water molecules associated with the cell walls. However, D'_{∞} and Δ_{∞} in a double exponential plot are not as clearly defined as those in a single exponential plot. One drawback of the NMR approach: the experiment is considerably more difficult when the water content is at the "natural" moisture level (e.g., 100% compared with the dry weight of wood). In that case, a larger percentage of the water is bound, which causes difficulty in separating the signal from bound water to that of "free" water, causing a sharp decrease of the apparent T_2 (and of T_1 as well in some cases) and thus increase of the linewidth of the water signal.

The NMR diffusion determination of the apparent size of cells in wood can be used to study the decay in wood. Decay in wood is a result of the breakdown of cell walls, thus causing an increase in the average size of the cells. Decay in wood will likely increase the distribution of sizes in the cells significantly. A correlation between the cell-size measurement and other quantitative measures of decay, such as mechanical properties of the wood samples, should be made in conjunction. Wood with significant decay usually has much higher water content, sometimes as high as 1,000% of the dry weight. Therefore, the concerns on the experimental difficulties at low

moisture level should not become an important issue. Studies along this direction are underway in our laboratory.

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