

## 185. Investigation of Water Dynamics in a Model Cellulosic System

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<http://www.ornl.gov/science-discovery/clean-energy/research-areas/systems-biology/bioenergy/dynamic-visualization-of-lignocellulose>

**Project Goals:** Lignocellulosic biomass comprises the vast majority of biomass on Earth and has the potential to play a major role in generation of renewable biofuels if cost-effective conversion can be achieved. Largely composed of plant cell walls, it is a complex biological composite material that is recalcitrant to the structural deconstruction and enzymatic hydrolysis into sugars that is necessary for fermentation to bioethanol. The Scientific Focus Area in Biofuels is developing “Dynamic Visualization of Lignocellulose Degradation by Integration of Neutron Scattering Imaging and Computer Simulation” for multiple-length scale, real-time imaging of biomass during pretreatment and enzymatic hydrolysis. This is providing fundamental information about the structure and deconstruction of plant cell walls that is needed to drive improvements in the conversion of renewable lignocellulosic biomass to biofuels.

Knowledge of water dynamics and structure at cellulose surfaces is important to understand how pretreatment regimes alter cellulose structure and how cellulases bind to cellulose interrupting hydrogen bonding between cellulose chains as a first step in cellulose hydrolysis. Quasi-elastic neutron scattering measures the local motions of H atoms on a pico- to nanosecond timescale and is used for characterizing water dynamics on surfaces. We report on measurements performed using deuterated bacterial cellulose equilibrated with H<sub>2</sub>O. Deuterium-labeling of cellulose strongly attenuates its scattering signal revealing the scattering contribution of water associated with the fibers providing insight into the dynamics of water surrounding cellulose fibers with unprecedented detail. Our results show that at lower temperatures the surface water gradually becomes glass-like, shows progressively slowing down dynamics, which could no longer be observed with the resolution of our experiment below about ~220K. The temperature dependent elastic intensity scans of deuterated cellulose hydrated in H<sub>2</sub>O reveal at least two populations of water present near the surface of the hydrated cellulose; “surface water” confined on the surface of the cellulose fibrils that becomes appreciably mobile at ~220K and “interfibrillar water” present in nanoscale water pockets between cellulose fibrils that becomes mobile at ~250K. Based on our analysis of the elastic scan data, three temperature points, 230, 250K and 265K, were chosen for a more detailed study of the dynamics of the system. The 230K data set probes the dynamics of the surface water, which at this temperature does not display long-range translational diffusion. It becomes translational in the 250K data set, while the interfibrillar water is still frozen contributing only an elastic scattering signal. Finally, at 265K the melting of the interfibrillar water dominates the 265K spectra. The diffusion coefficients of the water at 250K and 265K were  $0.85 \pm 0.04 \times 10^{-10} \text{ m}^2\text{sec}^{-1}$  and  $1.77 \pm 0.09 \times 10^{-10} \text{ m}^2\text{sec}^{-1}$ , respectively. This indicates that the water associated with cellulose is somewhat restricted compared to bulk super cooled water at 268K which has a self-diffusion coefficient  $9.41 \times 10^{-10} \text{ m}^2\text{sec}^{-1}$ . This study provides new insight into the dynamics of water surrounding crystalline cellulose and will aid in developing models to understand the mechanism of cellulose breakdown and its interaction with water, acids, and cellulases in an effort to optimize the cellulose digestion process.

Reference

1. W. S. Price, H. Ide, and Y. Arata, Y., “Self-Diffusion of Supercooled Water to 238 K Using PGSE NMR Diffusion Measurements,” *J. Phys. Chem. A* 103, 448–450 (1999).

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