# SIMULATION STUDIES OF THE WETTING OF CRYSTALLINE FACES OF COTTON CELLULOSE Pradeep Venkataraman Hank Ashbaugh Department of Chemical and Biomolecular Engineering Tulane University New Orleans, LA Glenn P. Johnson

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#### **Abstract**

Models of the surfaces of nano-sized cellulose crystals were constructed and a model droplet of water was placed on each. Then, the model atoms were given motion that corresponds to room temperature (a molecular dynamics simulation), and the spreading of the water over the surfaces was studied. Besides the surfaces that would be found for native cellulose, surfaces were also constructed with varying amounts of methyl groups that replaced the hydroxyl groups. Those methylated surfaces were devised as a start to understanding treatments of cotton fabrics for moisture management. The water was not expected to be so attracted to those groups, and that was the case. Although the water droplet did not spread out so much on the heavily methylated surfaces, it did bridge small regions of methylated cellulose. When the cellulose was completely methylated, the water droplet retained much of its original shape, and contact angles could be estimated for the water on the more heavily methylated surfaces. For the native cellulose crystals, however, the water spread out so that a partial monolayer was formed. Not enough water molecules were in the droplet to completely cover the surface.

#### **Introduction**

Cellulose is a common organic compound in nature. It is one of the basic structural constituents of the plant cell and constitutes 95% or so of the cotton fiber. Structurally, cellulose consists of linear chains of D-glucose units connected by glycosidic bonds to form polymeric chains through a condensation reaction. The hydroxyl groups on one polymer chain form hydrogen bonds with other chains resulting in crystalline structure. Different morphologies of cellulose crystal are present in nature, the most important being I $\alpha$  and I $\beta$ . I $\alpha$  is usually present in lower plant cells and algae, while the I $\beta$  allomorph constitutes the secondary wall of cotton fiber and other higher plants. Although the cellulose crystal structure was studied as early as 1913, it was not completely solved until 2002 when Nishiyama et al. (2002) used a combination of X-ray and neutron diffraction techniques.

Cotton at room temperature contains  $\sim 5$  wt% water and studies have shown that a moist cotton fiber (7-10 %) is stronger than a dry fiber (< 5%). This is attributed to strengthening of hydrogen bonds between the cellulose chains in presence of water. However, the presence of water in cotton is not always desirable for commercial reasons. The interactions of water with cellulose is difficult to image. However, a molecular level understanding of heterogeneous characteristics of the interaction of various faces of cellulose crystal with water is necessary to optimize and control the moisture in cotton. With potential applications in self-cleaning and fast-drying fabrics, chemical modification of cellulose could be better achieved by understanding the effects of these alterations on hydrodynamic behavior at molecular level.

Molecular dynamics (MD) simulations could be used as an effective tool for the aforementioned purpose. The length scales realized in MD simulations are of the order of few nanometers. Interfacial behavior of water at these length scales, measured mainly through contact angles, is influenced by line tension effects. Those effects could be mitigated by studying systems of various sizes. Despite the effects of system size, contact angles at the nano scale offer a close approximation at microscopic level. We present here the preliminary results of MD simulations of water molecules on (110) and (1-10) surfaces of I $\beta$  cellulose.

### **Materials and Methods**

### **Computational methodology**

#### **Structure**

The initial cellulose superlattice structure had 9 X 9 chains of cellulose consisting of 20 residues. This superlattice had its crystallographic (100) planes parallel to the X-Z plane. The crystal structure was rotated using a rotation matrix to make the (110) surface perpendicular to Z axis. The unit cell was identified and 2 layers of this surface made of 20 cellulose chains each consisting of 20 residues (GLYCAM Residue - 4GB) were generated. The end residues in the original PDB format file (GLYCAM Residue - 0GB) were replaced by the 4GB monomer to simulate infinite chains. 1000 water molecules were packed in a cubic box (specific gravity  $\sim 0.7$ ) were created using PACKMOL (Martinez et al., 2009) and initially placed at a distance of 3 Å from the surface.

# **Computational details**

The GLYCAM-06 empirical force field parameters (Kirschner et al., 2008) that are usually used with the AMBER program were transferred to the GROMACS program (van der Spoel et al., 2005) because it provides for an essentially infinite array. The Glycam\_06c FF was used to describe the 4GB residues, and the TIP4P-Ew model was used to define water. The structure was energy minimized using the steepest descent algorithm in GROMACS 4.05 until the maximum force was smaller than 100 kJ mol-1 nm-1. The heavy atoms (C1-C6, O4 and O5) of the 4GB residues were position-restrained with a force constant of 1000 kJ mol-2 nm-1 in each direction. The periodicity of residues was allowed to simulate an infinite surface. GROMACS 4.05 was used to carry out isochoric (constant volume) simulations at 1 bar and 300 K. Periodic boundary conditions in all directions were allowed. However, the box dimension in the Z direction was always greater than the cut-off distance of 9 Å for both vdW and electrostatic interactions. Long range corrections were included. Bonds involving hydrogen were constrained using the LINCS algorithm. The system was allowed to equilibrate for 1 ns using a Berendsen thermostat. The system was further relaxed using the Nose-Hoover thermostat for another 10 ns.

### **Hydrophobicity**

Hydrophobicity was introduced by creating a new residue (named XXX), where O2, O3 and O6 of 4GB residues were replaced by methyl groups. The partial charges were calculated using the RESP method (Bayly et al., 1993) on a geometry that was optimized by the HF/6-31G\* level of theory, averaged over 165 orientations. The charges on hydrogen atoms were lumped into associated heavy atom, as in case of 4GB residue. Glycam\_06c FF was used to describe the interaction parameters for atoms in XXX. The 4GB residues on a 20 residue chain were then systematically replaced by XXX residues to create 25%, 50%, 75% and 100% modified surfaces.

#### **Results and Discussion**

Figure 1a shows that water molecules spread out on an unmodified (110) surface. It is evident that the hydroxyl groups exposed on the (110) surface form hydrogen bonds with the water oxygen causing the spreading. The radial density profile, which is the density of water molecules from the center of mass of the droplet as a function of radial distance (Figure 1b), shows even density on the surface, further confirming the observation. The metrics to quantify the effect are still being formulated at this time but the qualitative analyses reveal that both (110) and (1-10) surfaces are largely hydrophilic. However, the way water spreads on the two surfaces is different and is not quantified. Also, the number of water molecules required to form a monolayer for the given surface area is greater than 1000 and hence we do not see monolayer coverage.



Figure 1a. Water droplets spreading on (110) surface

In contrast, the radial density profiles of the 100 % modified surface (Figure 2) show a spherical droplet profile. This is representative of a hydrophobic surface. A hydrophobic contact angle could be calculated by fitting a spherical profile to the equimolar surfaces of the water droplet. A similar effect is also observed on the (1-10) surface.



**Figure 1b.** Radial density profile of water on unmodified (110) surface. Y axis is the height in angstrom and X axis is the radial distance from the center of mass of droplet.



**Figure 2.** Radial density profile of water on (110) surface with all –OH groups replaced with –CH<sub>3</sub> groups.

At this time, we speculate that qualitatively both the (110) and the (1-10) surfaces are hydrophilic and could be chemically modified to alter the wetting behavior. The height of the droplet as a function of degree of substitution of hydroxyl groups on the surface (Figure 3) is reflective of the fact that the contact angle of water changes from a complete spreading situation to a highly hydrophobic one on both (110) and (1-10) surfaces. Hence, it is safely speculated that it is possible by chemical substitution to control the moisture on the primary cell wall of cotton.

### **Summary**

This effort conducted molecular dynamics simulations of the movement of water molecules that were initially in droplets poised above surfaces that corresponded to either native cellulose crystallites or crystalites that had been chemically modified to make the surfaces hydrophobic. These model water droplets dispersed in the case of the native cellulose with its hydroxyl groups, but retained much of the original droplet designation when on the fully methylated surfaces. The water molecules were able to bridge the methylated glucose residues if native structures were available in the vicinity, but the greater the substitution with methyl groups, the taller the droplet.



**Figure 3.** The height of droplet as a function of percentage replacement of the hydroxyl groups.

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