Traction-separation laws and stick-slip shear phenomenon of interfaces between cellulose nanocrystals

*Robert Sinko, Sinan Keten**

Dept. of Civil and Environmental Engineering and Dept. of Mechanical Engineering,
Northwestern University, 2145 Sheridan Rd., Room A136, Evanston, IL 60208.

*Corresponding Author: s-keten@northwestern.edu

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Abstract:

Cellulose nanocrystals (CNCs) are one of nature's most abundant structural material building blocks and possess outstanding mechanical properties such as a tensile modulus comparable to Kevlar. It remains challenging to upscale these properties in CNC neat films and nanocomposites due to the difficulty of characterizing interfacial bonding between CNCs that govern stress transfer under deformation. Here we present new analyses based on atomistic simulations of shear and tensile failure of the interfaces between I β CNCs in elementary fibrils, providing new insight into factors governing the mechanical behavior of hierarchical nanocellulose materials. We compare the two most relevant crystal surfaces and find that hydrogen bonded surfaces have greater tensile strength compared to the surfaces governed by weaker interactions. On the contrary, shearing simulations show that friction between the atomic interfaces depends not only on surface energy but also the energy landscape along the shear direction. While being a weaker interface, the intersheet plane exhibits greater energy barriers to shear. The molecular roughness of this interface, characterized by a greater energy barrier, exhibits a stick-slip deformation behavior as opposed to a continuous sliding mechanism observed for the interfaces with hydrogen bonds. Analytical models to describe the energy landscapes are developed using energy scaling relations for van der Waals surfaces in combination with a modification of the Prandtl-Tomlinson model for atomic friction. Our simulations pave the way for tailoring hierarchical CNC materials by taking a similar approach to techniques employed for describing metals, where mechanical properties can be tuned through a deeper understanding of grain boundary physics and nanoscale interfaces.

Graphical Abstract:

1. Introduction

Cellulose is the most abundant biopolymer on the planet(Fratzl and Weinkamer, 2007) and is found as a biological building block within a number of organisms including plants, tunicates, and bacteria. Within these systems, it provides natural solutions to achieving high strength and toughness ranging in scope from gels secreted by bacteria(Iguchi et al., 2000) to the trunks of trees(Moon et al., 2011). The impressive mechanical properties of crystalline nanocellulose rival those of synthetic aramid fibers(Diddens et al., 2008; W.D. Callister, 1994), while also being optically transparent when incorporated into composites(Ifuku et al., 2007; Iwamoto et al., 2005) and possessing a very low coefficient of thermal expansion comparable to that of carbon nanotubes(2005; Nishino et al., 2004). Further, cellulose can be chemically extracted(Hubbe et al., 2008) in a variety of shapes and sizes at a fraction of the cost of the production of structural, synthetic polymers. Utilizing natural nanocellulose in novel man-made materials is a growing area of research due to its natural abundance, low cost, outstanding mechanical properties(Diddens et al., 2008; Eichhorn, 2012; Matthews et al., 2006; Tanaka and Iwata, 2006), and high compatibility with synthetic polymers through simple surface modifications(Lee et al., 2009).

Research on nanocellulose has focused on a broad range of material systems including all-cellulose neat films and self-reinforced cellulose nanocomposites, as well as nanocomposites where nanocellulose particles can serve as a filler phase(Abbott and Bismarck, 2010; Dong et al., 2012; Eichhorn et al., 2010; Lee et al., 2012; Shanmuganathan et al., 2010). Recent studies have shown that the inclusion of cellulose nanocrystals (CNCs) within a polymer matrix or nanofiber significantly improves a number of material properties including the glass transition temperature, storage modulus(Dong et al., 2012), and transmittance of light(Iwamoto et al., 2005). However,

nanocomposites synthesized so far exhibit properties well below the upper bound suggested by traditional composite theories(Moon et al., 2011). This is primarily attributed to weak interfaces between host and filler materials (i.e. CNCs and polymer) or multiple filler structures (i.e. multiple CNCs), which are crucial to the performance of the macroscale material. Specifically, interfaces can help to promote percolated networks between filler particles(Mizuno et al., 2013) and also help to distribute cracks within the material(Ohji et al., 1998). The response of these percolated interfaces to water can also give rise to stimuli-responsive materials that undergo sharp transitions in their elastic properties at given moisture content(Capadona et al., 2008; Shanmuganathan et al., 2010).

Beyond CNC-polymer composites, all-cellulose films provide insight into the importance of CNC interfaces within these materials. Bacterial cellulose gels have been shown to be exceptionally strong as a result of significant hydrogen bonding between fibrils(Iguchi et al., 2000; Lin et al., 2012). Additionally, recent experiments have shown that increasing the alignment and consequently the size and number of CNC-CNC interfaces gives rise to improved mechanical performance as a results of better load transfer between the crystals(Reising et al., 2012). Based on these observations, it is clear that interfaces between CNCs govern a large range of properties in both neat films and CNC-polymer composite systems.

Recent studies have been conducted on CNCs to understand the molecular mechanisms that help to stabilize the crystalline morphology and provide strength to these nanostructures. Through a combination of computational(Dri et al., 2013; Kulasinski et al., 2014; Sinko et al., 2014; Wu et al., 2013) and experimental(Kong and Eichhorn, 2005; Lindman et al., 2010; Nishiyama et al., 2002; Tashiro and Kobayashi, 1991) studies, it has been established that both hydrogen bonding and secondary van der Waals interactions play a crucial role in determining

the emergent macroscale properties of these crystals. For I β cellulose, commonly called “natural” cellulose, it has been shown that hydrogen bonding is dominant along the (110) plane while van der Waals interactions are dominant along the (200) plane (Sinko et al., 2014), with these planes indicated in Figure 1A. These studies also suggest that crystals must be a few nanometers in cross-sectional dimensions in order to maximize their fracture surface energy and minimize surface to volume ratio (Sinko et al., 2014) – a critical aspect of optimal fillers for nanocomposites or neat films (Schadler, 2004). This optimal size, predicted to be 5-7 nm is both height and width (Sinko et al., 2014), emerges from the interplay between the fracture surface energy and surface area. Smaller nanocrystals exhibit lower fracture surface energy, whereas larger crystals have reduced surface area to volume ratio, making this intermediate length-scale optimal for nanocomposites.

Figure 1: (A) Cross-section of a I β CNC consisting of 36 cellulose chains in a hexagonal arrangement with the (200) and (110) surfaces exposed as indicated and showing the simulation width dimension of 5.39 nm. (B) Axial view of a I β CNC that includes the simulation fibril height of 2.97 nm and range of fibril lengths. In simulation, three different fibril lengths of 5.19 nm (5 repeat units), 10.38 nm (10 repeat units), and 15.57 (15 repeat

units) are used. Snapshots of the (C) (110)-(110) interface and (D) (200)-(200) interfaces between two CNCs that are studied in this work. (E) Schematic showing the directions of interfacial separation and interfacial shearing (traction). The blue atoms are the carbon atoms that are fixed during SMD simulation and the orange are the SMD atoms (carbon, oxygen, and hydrogen) that are pulled during simulation.

While a number of recent studies have characterized the elastic and fracture properties of crystalline cellulose at the molecular level (Eichhorn and Davies, 2006; Kulasinski et al., 2014; Matthews et al., 2006; Sinko et al., 2014), the focus has been on the axial and transverse tensile properties of individual CNCs. Much less is known about interfaces between multiple CNCs, or shear failure of CNCs under various loading scenarios relevant to nanocomposites and neat films (Chen et al., 2009; Cox, 1952; Gao and Li, 2005). Without knowing these interfacial properties, a key bottleneck arises as it is difficult to understand nanoscale interfacial failure mechanisms that arise at the grain boundaries of CNCs in neat films, and also in polymer nanocomposites (Mazeau and Vergelati, 2002). Molecular level studies of interfacial mechanics are fundamentally important to establish a materials-by-design approach to making high-performance cellulosic materials such as cellulose neat films (Reising et al., 2012), CNC-polymer nanocomposites (Dong et al., 2012; Lee et al., 2012; Moon et al., 2011; Shanmuganathan et al., 2010), and all-cellulose composites (Abbott and Bismarck, 2010; Nishino et al., 2004).

As a first step to improving the performance of these materials by elucidating their molecular mechanisms of failure, here we focus on the most common polymorph of cellulose, referred to as I β cellulose forming the crystalline domains of elementary fibril structures in wood, shown in Figure 1A and 1B. It should be noted that although the I β cellulose structure is used, the results could be extended to other polymorphs such as I α cellulose or cellulose II that have similar surface characteristics but different crystalline organization of cellulose chains. The focus of this study is to characterize the two prominent interfaces, the (110)-(110) (Figure 1C) and (200)-

(200) (Figure 1D), between CNCs in order to provide insight into their mechanical behavior in larger-scale polycrystalline or entangled CNC assemblies. Whereas previous work(Wu et al., 2013) has focused on pure sliding between CNCs on a periodic substrate of crystalline cellulose, our work focuses on understanding the interfacial failure between finite CNCs in both separation and traction(Park and Paulino, 2013) failure modes using molecular dynamics simulation coupled with analytical modeling.

2. Materials and Methods

2.1 Cellulose nanocrystals structure

The interfaces between crystalline domains extracted from so-called cellulose elementary fibrils (cellulose nanocrystals consisting of 36 individual cellulose chains arranged in a hexagonal shape)(Habibi et al., 2010) are explored using molecular dynamics simulations. The cross-sectional dimensions (5.39 nm in width and 2.97 nm in height) of elementary fibrils were determined to be the most relevant crystalline structure as they are the most common shape observed upon extraction from plants(Moon et al., 2011) and close in size to the recently predicted optimal size of 5-7 nm in height and width on the basis of scaling of the fracture surface energy and surface area with nanocrystal size(Sinko et al., 2014). Figure 1A shows the cross-section and hexagonal arrangement of cellulose chains in an elementary fibril, with the (110) and (200) surfaces indicated. Figure 1B shows another perspective of the CNCs in elementary fibrils and indicates the length dimensions used in this study. For this study, three different fibril lengths were studied with chain lengths of 5, 10, and 15 cellulose repeat units corresponding to fibril lengths of 5.19 nm, 10.38 nm, and 15.57 nm. Results are included within the manuscript for 5.19 nm fibrils (separation and shearing along the width) and 10.38 nm fibrils (shearing along the length). The remaining simulations results for the other fibril lengths are

shown in Figures S1-S4 of the Supplemental Information. The simulations and subsequent analyses conducted in this work focus on the (110)-(110) interface (Figure 1C) and the (200)-(200) interface (Figure 1D) that are believed to be the most common between cellulose fibrils aligned along their length. They are believed to be the most common based on the observed self-assembly behavior of CNCs in the liquid crystalline state that form pronounced chiral nematic patterns (Habibi et al., 2010; Mu and Gray, 2014) and further due to stark differences between the (110) and (200) surfaces including their geometry and polarity. Although mixed contact between (110) and (200) surfaces is physically possible, it is unlikely due to the aforementioned differences in surface geometry and chemical characteristics.

2.2. Steered molecular dynamics (SMD) simulations

Molecular dynamics simulations were conducted using the NAMD molecular dynamics package (Phillips et al., 2005) and the CHARMM force field for carbohydrates (Brooks et al., 1983; Raman et al., 2010). In order to characterize these interfaces and develop traction-separation potentials (Park and Paulino, 2013) for failure at these interfaces, a steered molecular dynamics (SMD) technique (Park et al., 2003) was utilized to separate the fibrils in two directions; 1) normal to the interface (i.e. separation) and 2) parallel to the interface (i.e. traction or shearing) with the specific pulling directions used to cause these failure modes indicated in Figure 1E. Initial system configurations were generated using the cellulose-builder toolkit (Gomes and Skaf, 2012) and psfgen tool in VMD (Humphrey et al., 1996), with the fibrils oriented such that the x-direction was normal to the interfaces and the y-direction was parallel to the interfaces. Before conducting SMD simulations, systems were equilibrated for 1.0 ns under an NVT ensemble at a temperature of $T = 298$ K. During equilibration, the positions of the carbon atoms in the leftmost fibril were constrained in the y-direction in order to prevent twisting

of the fibrils (blue atoms in Figure 1E). Although cellulose fibrils tend to have an angle of twist of $1.5^\circ/\text{nm}$ (Eichhorn and Davies, 2006; Zhao et al., 2013), the simulations aimed to limit this effect in order to decouple twisting effects from the interfacial separation and shear behavior.

After the system energy was minimized during equilibration, multiple snapshots of the system were taken every 100 ps and used as starting conformations for SMD simulations since multiple initial configurations of the system are necessary to calculate the average work describe the free energy differences (Jarzynski, 1997; Park et al., 2003) for this nonequilibrium simulation and associated failure process. SMD simulations employed a virtual atom velocity of $0.0002 \text{ \AA}/\text{fs}$ (2 m/s) and a relatively high spring constant of $4000 \text{ kcal/mol- \AA}^2$. A high spring constant and low pulling velocity were chosen in order to reduce oscillations and noise of the pulled atoms, while also providing computational efficiency and better sampling. The effect of varying these parameters was also examined in order to alleviate concerns about rate dependence and a brief discussion is included in the Supplemental Information. Simulations were conducted until the interfaces experienced complete failure (i.e. plateau in energy landscape at 0), with simulations lasting between 0.6 – 8.0 ns depending on the type of failure (separation vs. traction), specific interface, and fibril dimensions. During SMD simulations, carbon atoms in the leftmost fibril were fixed and the separation or traction force was applied to all atoms in the pulled crystal using the tethered, virtual SMD atom. Further, these atoms were constrained to move only in the pulling direction in order to reduce unwanted effects such as peeling and simulate only the intended interfacial separation.

For each set of SMD simulations, five (separation simulations) or ten (traction simulations) unique starting trajectories were used and the potential of mean force (PMF) is constructed by integrating the force-displacement curve from the failure process. An exponential average (Park

et al., 2003) of the results from each different starting trajectory is used for all simulation analyses(Jarzynski, 1997). Hydrogen bond analyses were conducted using system trajectories in VMD with a cutoff distance of 4.0 Å and cutoff angle of 50°. These values are often reported as an upper limit for the development of hydrogen bonds(Desiraju, 1996) and are chosen as the cutoffs here in order to capture all possible hydrogen bonds developed during simulations.

3. Results and Discussion

3.1 Separation of CNC interfaces

Here we present results of separation and traction SMD simulations of CNC-CNC interfaces to characterize their behavior and explain how these interfaces will influence larger scale systems such as CNC neat films. The first set of SMD simulations conducted were separation simulations for both the (110)-(110) and (200)-(200) interfaces. The resulting work-displacement curves for each interface are shown in Figure 2A and 2B for a fibril length of 5 repeat units (5.19 nm). Based on earlier findings, it is hypothesized that the (110)-(110) interface should be dominated by hydrogen bonding(Kong and Eichhorn, 2005; Nishiyama et al., 2002), while the (200)-(200) interface should be stabilized primarily by van der Waals interactions(Dri et al., 2013; Sinko et al., 2014). Therefore, since hydrogen bonding is stronger than weak secondary interactions, it is anticipated that the (110)-(110) interface should have a higher fracture energy than the (200)-(200) interface. The results shown in Figure 2A and 2B support this hypothesis, indicating that the energy required to separate the (110)-(110) interface (~5800 kcal/mol for a 5.19 nm fibril) is nearly twice that required for the (200)-(200) interface (~2800 kcal/mol for a 5.19 nm fibril).

Figure 2: (A) Work vs. displacement curve obtained from SMD simulation of separating the (110)-(110) interface of two CNCs and (B) work vs. displacement curve obtained for the (200)-(200) interface. The gray curves show results for five unique SMD simulations with different starting trajectories and the red-dotted line shows the exponential average of multiple runs. The black, dashed line represents the fit of the model proposed to describe this energy landscape of the form $E_v(x) = -\Delta F/(1+ax^2)$ where ΔF is the change in energy between the equilibrium and separated states. (C) The contributions to the total fracture energy for the (110) interfaces (averaged for all fibril lengths) are dominated by non-bonded, electrostatic interactions. (D) On the other hand, (200) interfaces are dominated by contributions from non-bonded, van der Waals interactions. The relative differences in the electrostatic energy contributions, both in magnitude and percentage of the total energy, help to explain the observed differences in the fracture energies between the two surfaces.

The free energy landscapes for the interfacial separation in Figure 2 provide a clear picture of how the interfacial energy changes as a function of separation distance. However, it is also useful to simply look at the free energy difference, ΔF , between the equilibrated and separated states as this provides a single numerical value to describe the interfacial strength/adhesion. Because the total interfacial area influences the free energy difference, the work of separation per unit area, or the fracture surface energy, G , is a more useful metric and is simply the free energy difference normalized by the interfacial area ($\Delta F/A$). The fracture energies and interfacial areas for the two interfaces for all fibril lengths are provided in Table 1. The results show that the fracture surface energy of the (110)-(110) interface is nearly twice that of the (200)-(200) interface with $G = 5.0 - 5.5 \text{ kcal/mol-}\text{\AA}^2$ (3-4 J/m²) for the (110)-(110) compared to $G = 2.0 - 2.3 \text{ kcal/mol-}\text{\AA}^2$ (1.5-1.8 J/m²) for the (200)-(200). The results of Table 1 indicate that there is little to no size dependence (Keten et al., 2010) (only examined in this study in terms of the length of the fibrils) as the fracture surface energy, that is, work of separation per unit area, is approximately constant for all lengths. This suggests that the system sizes studied here are beyond the critical length scale below which fibril length plays a role on the computed energies. This finding indicates that our previous size-dependence observations can be generalized for different crystal surfaces (Sinko et al., 2014).

Table 1: Comparison of calculated fracture energies and hydrogen bond densities for (110)-(110) and (200)-(200) interfaces. The fracture energy of the (110)-(110) interface is significantly larger than that for the (200)-(200) interface and can be explained by the significantly higher number and area density of hydrogen bonds that are developed across the interfaces.

Interface	Fibril Length, Repeat Units (nm)	Interfacial Surface Area, Å ²	Fracture surface energy, kcal/mol- Å ² (J/m ²)	Average Number of Hydrogen Bonds at Interface	Area Density of Hydrogen Bonds (Å ⁻²)
(110)-(110)	5 (5.19)	1219	4.75 (3.30)	45	0.0369
	10(10.38)	2437	5.61 (3.90)	103	0.0423
	15 (15.57)	3656	5.48 (3.81)	170	0.0465
(200)-(200)	5 (5.19)	1064	2.62 (1.82)	8	0.00752
	10(10.38)	2128	2.64 (1.83)	15	0.00705
	15 (15.57)	3192	2.38 (1.65)	24	0.00752

The drastic difference in fracture energies for the two interfaces can be attributed to the disparity of dominant molecular interactions along the specific surfaces, most notably, hydrogen bonding. In order to verify this hypothesis, two approaches are taken. First, the average number of hydrogen bonds at the interface was calculated during system equilibration. The results are shown in Table 1 and indicate that the total number of hydrogen bonds is greater for the (110)-(110) interface compared to the (200)-(200) interface. However, since the interfaces are of different size, an area density of hydrogen bonds for each interface is calculated. These values indicate that the area density of hydrogen bonds is nearly an order of magnitude larger for the (110)-(110) interface. Given the stronger nature of hydrogen bond interactions compared to the van der Waals dominated (200)-(200) interface, this difference likely governs the larger fracture surface energy of the (110)-(110) interface.

The second approach to explain these differences is to break down the total fracture energy into contributions from non-bonded electrostatic interactions and non-bonded van der Waals interactions across the interface. Figure 2C and 2D show the contributions from these two components for each surface. For the (110) interfaces in Figure 2C, we see that the electrostatic contributions, which are directly correlated with the number of hydrogen bonds developed across the interface, account for roughly 54% of the total fracture energy. However, for the (200) interfaces, these electrostatic contributions account for only 33% of the total fracture energy and

are much smaller in their absolute magnitude (0.58 J/m^2) compared to the (110) interfaces (1.99 J/m^2). These results again support the notion that increased electrostatic interactions (i.e. hydrogen bonds) for the (110) interfaces give rise to higher fracture energies compared to the (200) interfaces.

3.2 Analytical model for CNC interfacial separation potentials

The fracture surface energy provides a simple metric for quantifying the strength of this interfacial separation, but neglects the shape of the energy landscape, or in other words the characteristics of the so-called separation law. The distance decay function of the energy landscape is important for describing the colloidal interaction between these two fibrils in the context of a multi-scale framework. Based on the results of SMD interfacial separation simulations for both the (110)-(110) and (200)-(200) interfaces, an analytical model is proposed to represent the shear energy landscape. Although a different molecular mechanism is dominant for the two interfaces (hydrogen bonding vs. van der Waals interactions), Figure 2 demonstrates that the distance scaling of the free energy for the separation process is similar for the two interfaces. This similarity suggests that despite the different hydrogen bond density characteristics of (200) and (110) surfaces of CNCs in elementary fibrils shown in Table 1, the interfaces can be modeled using a similar function. Considering that van der Waals interactions are the underlying molecular interaction for both interfaces, we can simplify the modeling of this interface if we treat the two surfaces as flat, parallel plates. The van der Waals interaction energy E_v between two parallel, flat plates separated by a distance x is given by (Israelachvili, 2010):

$$E_v(x) = -\frac{H}{12\pi x^2} \quad (1)$$

where H is the Hamaker coefficient that defines the attraction between two surfaces in a specific medium. This expression indicates that the van der Waals interaction energy is

proportional to the inverse square distance between the two plates. Considering only the attractive part of the effective potential between surfaces, and assuming that the energy goes to $-\Delta F$ at the point $x = 0$ one can rewrite this equation as:

$$E_v(x) = \frac{-\Delta F}{1 + ax^2} \quad (2)$$

where ΔF is the difference in free energy between the equilibrated and separated states and $x = 0$ is the equilibrium distance between surfaces. The fitting parameter a in Eq. (2) depends on the interfacial geometry, and the Hamaker coefficient of the particular material. When implementing this potential in a multi-scale framework, the repulsive portion of the potential must also be included. By changing the equilibrium position of the surfaces to be at $x = r_0$ and assuming the repulsive and attractive potentials are of a similar analytical form, the potential can be rewritten as:

$$E_v(x) = \frac{-\Delta F}{1 + a(x - r_0)^2} \quad (3)$$

This analytical expression is fit to the SMD simulation results for both interfaces with specific parameter values based on a least-squares regression included in Table S1 of the Supplemental Information. This best-fit curve for the (200)-(200) captures the simulation results well, with a goodness of fit statistic of $r^2 = 0.992$ as shown in Figure 2B. The model in Eq. (3) was derived for surfaces interacting with purely van der Waals interactions and does not take into account the significant interfacial hydrogen bonding of the (110)-(110) interface. Regardless, given the similar shape of the energy landscape compared to the (200)-(200) interface, this model was fit to the (110)-(110) interface data and as shown in Figure 2A, the model fits remarkably well for this interface with a goodness of fit statistic of $r^2 = 0.994$. This indicates that hydrogen bonding does not change the distance scaling of the energy landscape appreciably, but solely serves as a

strengthening mechanism for the interface at short distances. This is further evidenced by the fact that the fitting parameter a is approximately constant for both interfaces and all lengths with an average value of $a = 1.38$. These similarities are somewhat expected since hydrogen bonds are implicit in the CHARMM force field, but still interesting in the sense that adding hydrogen bonding (through increased electrostatic interactions that exhibit different distance scaling) does not change the distance scaling of the energy landscape. Finally, when comparing fitting parameters for different lengths, we notice that the value of ΔF when normalized by the length is approximately constant and has a value of ~ 1790 kcal/mol-nm for the (110) interfaces and ~ 730 kcal/mol-nm for the (200) interfaces.

3.3 Traction of CNC interfaces (width dimension)

The pure separation behavior of CNCs is not adequate to capture the entire mechanical behavior of macroscale cellulose assemblies. Specifically, in bacterial cellulose films(Iguchi et al., 2000), nanocomposites(Dong et al., 2012; Moon et al., 2011), and other materials made up of CNCs, the strong interactions between the CNCs cause them to form larger-scale networks where load is transferred primarily by the shear resistance between CNCs. Improved mechanical properties are obtained when contact between CNCs is increased by for instance shear-alignment(Reising et al., 2012), but a quantitative model for describing resistance to sliding at these crucial interfaces remains to be established. In the spirit of continuum micromechanics, it is customary to define interfaces with traction potentials of the form of the Tomlinson model(Popov, 2010) in addition to the separation potentials defined above. For this purpose, we investigate the traction portion of these potentials by performing shearing simulations along the width and length of the fibril. The results for the (110)-(110) interfacial shear simulations are presented in Figure 3A and the results for the (200)-(200) interface are shown in Figure 3B along

the width of the fibril. The shear mechanisms at play and energy landscapes are similar and exhibit a periodic form that couples local energy minima and maxima with an overall saturation of the energy to a final value. The behavior exhibited here is similar to slip-stick friction that is observed for the interactions between many materials (Karnopp, 1985; Yoshizawa and Israelachvili, 1993) and merits detailed examination in the context of polysaccharide nanocrystals.

The first important observation is that the periodicity of the shear energy landscapes can be directly related to the geometry of the specific surfaces. As shown in Figure 3A, there are five energy minima/maxima that correspond to each of the five chains at the interface. For the (110) surface, the chains have a spacing of 5.85 Å (Imai et al., 2003) and therefore should become aligned every 5.85 Å during the shearing process. The average distance between peaks in Figure 3A is calculated to be approximately 6 Å and indicates that the position of the energy minima/maxima is directly related to the surface geometry. This observation also holds true for the (200)-(200) energy landscape in Figure 3B as the peaks are located approximately 8.3 Å apart, which is nearly identical to the crystal dimension for intrachain spacing along the (200) surface of 8.2 Å (Imai et al., 2003). These observations are in good agreement with a recent study (Wu et al., 2013) where similar periodicity corresponding to molecular dimensions was observed in the force-displacement profile for sliding between a finite CNC and infinite substrate. Interestingly, one important trend that emerges is that the energy barriers are significantly higher for the (200)-(200) interface compared to the (110)-(110) interface, which can be explained by a further investigation into the shearing behaviors in section 3.4.

Figure 3: (A) Work vs. displacement curves obtained for SMD simulation of shearing the (110)-(110) interface of two CNCs with a length of 5 repeat units along the width of the fibrils. (B) Work vs. displacement curves obtained for SMD simulation of shearing the (200)-(200) interface of two CNCs with a length of 5 repeat units along the width of the fibrils. In both plots the gray curves represent energy landscapes for 10 individual simulations, the red, dotted curves represent the exponential average of these different cases and the blue, dashed curves represent the analytical model used to describe these energy landscapes.

3.4 CNC traction: stick-slip versus continuous sliding

Although the periodic trends in the energy landscapes for both interfaces shown in Figure 3 are similar, there are some differences that can be attributed to the dominant molecular interaction mechanism and varying surface characteristics. Most notably, for the (110)-(110) interface, there is a smooth transition between energy minima and maxima while the (200)-(200) interface exhibits a sharper transition consistent with stick-slip friction mechanisms observed for granular materials (Nasuno et al., 1998). These differences are even more pronounced when looking at the force-displacement curves (Fig. S5 and S6 in the Supplemental Information). For the (110)-(110) interface the force is smooth and sinusoidal as the fibrils are sheared, whereas the (200)-(200) interface exhibits a zigzag force vs. displacement profile. These findings indicate a transition from continuous sliding for the (110)-(110) interface to stick-slip friction characteristics for the

(200)-(200) interface. A recent experimental study on NaCl crystals corroborates this finding because a similar transition from continuous sliding to stick-slip has been observed as the shear energy barrier (also known as the corrugation energy) changes from 0.1 eV to 0.5 eV (Socoliuc et al., 2004). This transition is predicted by an order parameter, η , that is a function of the shear energy barriers, distance between energy barriers, and elastic modulus of the material. Specifically, assuming the modulus and distance between barriers are approximately equal, the order parameter scales directly with the magnitude of the energy barriers. For large values of this parameter (high energy barriers), stick-slip behavior is observed while low values of this parameter (low energy barriers) are indicative of continuous sliding. Shearing behaviors of the (110)-(110) and (200)-(200) fit well qualitatively within this framework as the order parameter for the (200)-(200) interface is much higher than the (110)-(110) interface due to a significantly higher energy barrier.

The continuous sliding exhibited by the (110)-(110) interface is particularly interesting when considering the dynamics of hydrogen bonding across the interface. Figure 4A shows the number of hydrogen bonds across the interface during the shearing of the fibrils, and Figure 4B provides illustrations of the proposed sliding mechanism. Although the interface is continuously sliding, there are changes in the energy due to breaking and reformation of hydrogen bonds during the shearing process. This breaking and reformation of hydrogen bonds is due to the alignment and misalignment of the cellulose sheets, specifically the hydroxyl groups, across the interface as the fibrils shear past one another. Further, the location of local maxima in the number of hydrogen bonds corresponds to the location of energy minima in Figure 3A and similarly for the hydrogen bond minima corresponding to energy maxima. On the other hand, the (200)-(200) stick-slip behavior cannot be attributed to hydrogen bonds as there are very few that exist across the

interface. Instead, molecular friction arising from sterical contacts between hydrogen and hydroxyl groups causes the sharper, more distinct stick-slip events. Additionally, the increased energies observed in the landscape of Figure 3B are attributed to polar/non-polar patches along the interface that are more energetically expensive to overcome than the all-hydrophilic (110) surface that exhibits significant hydrogen bonding.

Figure 4: (A) Hydrogen bonds along the (110)-(110) interface of CNCs as a function of the distance the fibrils have been sheared during simulation. The peaks in this plot correspond to the peaks in the energy landscape of Figure 3A indicating they are the cause of the observed stick-slip mechanism. (B) VMD snapshots and illustration of the shearing mechanism that is responsible for the shape of the energy landscape. During shearing of the (110)-(110) interface, hydrogen bonds break and reform and are responsible for the periodic nature of the energy landscape. Here, blue hydrogen bonds are between chains that are aligned at equilibrium (i.e. beginning of the shear simulations) and red hydrogen bonds are between chains that are misaligned at equilibrium.

3.5 Traction of CNC interfaces (axial dimension)

In addition to shearing along the width direction, simulations where fibrils were sheared along their length were performed (axial direction). The results for these simulations are shown in Figure 5 and demonstrate similar trends to those observed for shearing along the width direction.

The periodicity of the energy landscape is again dictated by the geometry of the surface with the energy minima/maxima spaced approximately 10.4 Å which corresponds with the CNC crystalline dimension along the length of the chain of 10.38 Å (Imai et al., 2003). Additionally, the difference between continuous sliding for the (110)-(110) interface and stick-slip behavior for the (200)-(200) interface is still observed. This finding ascertains that this phenomenon is indeed dictated by the underlying interaction mechanisms, and not the particular shearing direction.

Figure 5: (A) Work vs. displacement curves obtained for SMD simulation of shearing the (110)-(110) interface of two CNCs with a length of 10 repeat units along the length of the fibrils. (B) Work vs. displacement curves obtained for SMD simulation of shearing the (200)-(200) interface of two CNCs with a length of 10 repeat units along the length of the fibrils. In both plots the gray curves represent energy landscape for 5 individual simulations, the red, dotted curves represent the exponential average of these different cases and the blue, dashed curves represent the analytical model used to describe these energy landscapes.

3.6 Analytical model for CNC interfacial traction potentials

Although the overall qualitative shape and behavior is similar for both interfaces, some distinct differences in the energetics of sliding can be observed. As discussed previously, it is important

to analytically describe these landscapes as traction potentials that could be used to explain failure mechanisms of nanocomposites across different weak interfacial planes. Here we attempt to present a comprehensive description of these interfaces, and provide a few simplifications that will be helpful in generalizing the main characteristics of the model. First, it is assumed that local energy minima/maxima are equally spaced along the energy landscape. This enables the use of a periodic function to describe peak spacing but may neglect contributions of strain within the crystal that causes unequal spacing between peaks. Second, it is assumed that the magnitude of the energy barriers decays linearly with each subsequent barrier for the (110)-(110) interface and decreases exponentially for the (200)-(200) interface, which is suggested by the simulation data. This simply ensures an analytical function is used in the model, although a more complicated, exact description of energy barrier decay behavior could be implemented if the trends are not well defined. Overall, these simplifications allow for the development of a simple, physically informed model that is capable of describing the shear landscape of an arbitrary finite, rough surface with well-defined local maxima and minima based on the surface chemistry.

Figure 6: The model developed that analytically describes the energy landscape for fibril is observed to combine an energy saturation and oscillation term. (A) The energy saturation is due to the pure separation of the finite surfaces that make up the CNC-CNC interfaces from the equilibrium to separated states and can be approximated using a $1/y^2$ power law. (B) The oscillation term is governed by the roughness of the surfaces and the molecular interactions across the interfaces and can be described by the Prandtl-Tomlinson model for atomic friction when modified for a finite interface length. (C) The superposition of these two energy components results in an analytical model that can describe the shearing of any finite surface with periodic roughness.

The first aspect of the model to consider is the overall saturation behavior of the energy landscape that is similar to the separation potential observed for these fibrils in Figure 2 and illustrated in Figure 6A. For this portion of the model, the formula for the van der Waals interaction energy for two flat, parallel surfaces presented in Eq. (1) is utilized. The modification here is that the fibrils are not moved apart in the x direction (i.e. separation), but are rather moving their centers apart in the y direction (i.e. traction). We propose that the van der Waals interaction energy between the surfaces should not only scale with the separation distance between the surfaces, but also the radial distance between the geometric centers of the surfaces.

In this case, the interaction energy between the two surfaces would be given by Eq. (4) where r is the radial distance between the centers of the two surfaces

$$E_v(r) = E_v(x, y) = -\frac{H}{12\pi r^2} = -\frac{H}{12\pi x^2 + 12\pi y^2} \quad (4)$$

Therefore, since the separation between the surfaces is constant throughout the shearing process (i.e. constant value of the variable x), then the interaction energy of the two surfaces is simply a function of the shear displacement and constants ΔF_s , the change in free energy between the equilibrium state and the separated state after shearing, and a , a fitting constant

$$E_{v,sat}(y) = -\frac{\Delta F_s}{1 + ay^2} \quad (5)$$

In addition to the overall saturation in the energy landscape due to the distance scaling relation given by Eq. (5), the periodic local maxima and minima arising from the surface chemistry must be included in the analytical model. Previous studies have shown that friction between atomically rough surfaces has been described by the Tomlinson or Prandtl-Tomlinson model (Popov, 2010; Verhoeven et al., 2004) and this serves as the basis for the periodic component of the traction potential. The limitation of the traditional Tomlinson model is that it was developed for sliding over an infinite surface and does not take into account the finiteness of the interfaces used here and relevant to any system in which contact is lost during deformation of the interface. Therefore, a decay function must be included to account for the change of the energy barrier for each subsequent barrier as the size of the interface between surfaces is decreased. The results from SMD simulations also indicate that a sinusoidal function can capture the periodicity in the maxima/minima as suggested by the Tomlinson model and illustrated in Figure 6B. This periodic, oscillatory component of the energy landscape can be written analytically as

$$E_{v,per}(y) = -f_{decay}(y)E_{set} \cos\left(\frac{2\pi y}{d}\right) \quad (6)$$

Here, d is the distance between energy minima or maxima as governed by the geometry of the surface, E_{set} is the energy required to break one set of molecular interactions, and $f_{decay}(y)$ is the decay function that controls the change in the energy barrier due to the finite length of the fibrils. As discussed previously, it is found that a linear decay function best captures the (110)-(110) interface, whereas an exponential decay function can be used to model the (200)-(200) interface.

$$E_{v,per(110)}(y) = -E_{set} \left[\frac{4n+1}{8} - \frac{|y|}{2d} \right] \cos\left(\frac{2\pi y}{d}\right) \quad |y| \leq d \left(n + \frac{1}{4} \right). \quad (7)$$

$$E_{v,per(200)}(y) = -E_{set} e^{-c|y|} \cos\left(\frac{2\pi y}{d}\right) \quad |y| \leq d \left(n + \frac{1}{4} \right) \quad (8)$$

In Eq. (7), n is the total number of energy minima in the landscape (as governed by the surface chemistry), and in Eq. (8) c is a constant that controls the rate of decay of the energy barriers. Note here that the $|y|$ term is included such that the function represents shearing in either the positive or negative y -direction as the energy profile should be symmetric about the equilibrium configuration. Since we know that the total energy landscape of shearing the fibrils is a superposition of saturation behavior (Figure 6A and Eq. (5)) and periodic oscillations (Figure 6B and Eq. (7-8)), the total energy profile is simply a sum of the two components as shown in Figure 6C and given by Eq. (9A) and (9B) for the two interfaces:

$$E_{v(110)}(y) = -\frac{\Delta F_s}{1 + ay^2} - E_{set} \left[\frac{4n+1}{8} - \frac{|y|}{2d} \right] \cos\left(\frac{2\pi y}{d}\right) \quad |y| \leq d \left(n + \frac{1}{4} \right) \quad (9A)$$

$$E_{v(200)}(y) = -\frac{\Delta F_s}{1 + ay^2} - E_{set} e^{-c|y|} \cos\left(\frac{2\pi y}{d}\right) \quad |y| \leq d \left(n + \frac{1}{4} \right) \quad (9B)$$

The analytical models for the traction potential given above in Eq. (9) were fit to the SMD data in Figures 3 and 5 using physical parameters for the specific surfaces and adjusting fitting parameters as necessary. Although it appears there are a large number of fitting parameters in the

models, many of these quantities are obtained simply from the geometry of the interfaces, specifically the values of n and d . For the (110)-(110) interface along the width dimensions, $n = 5$ and $d = 6.0 \text{ \AA}$ and for the (200)-(200) interface along the width dimension (for the larger fibril used in simulation), $n = 4$ and $d = 8.3 \text{ \AA}$. For the fibrils sheared in the length dimension, both surfaces have $n = 10$ and $d = 10.4 \text{ \AA}$. The parameter E_{set} can be obtained by approximating the energy contribution of a single set of molecular interactions from the energy landscape. Therefore, the only true fitting parameters are a , which controls the rate of saturation of the energy landscape and c , which controls the rate of decay of energy barriers for the (200)-(200) interfaces. These fitting parameters can be obtained using a least-squares curve fitting protocols in Matlab and specific values of the parameters are included in Table S2 of the Supplemental Information. The goodness of fit statistics for these models are calculated to be $r^2 = 0.80 - 0.95$ for each of the four cases with each of the fits shown as blue, dashed curves in Figures 3 and 5. Cooperativity effects can also be captured using this model by simply changing the form of $f_{decay}(y)$ that reflects the trends in the energy barriers.

3.7 Prediction of CNC neat film properties using simulation and shear-lag model

Although these analytical functions themselves are useful for describing interactions between CNCs from a higher level, coarse-grained perspective, they can also provide new insight into previous experimental observations at the macroscopic level through multi-scale analyses. For example, a unique property of bacterial cellulose films is their ability to dissipate a lot of energy while maintaining a high modulus, making them intriguing materials for applications such as acoustics where deadening or blocking of sound is needed (Henriksson et al., 2008). An open question that remains is why these systems have high $\tan \delta$ values. Insight from our model suggests that the slip events along the hydrogen bonded interfaces can give rise to large energy

dissipation similar to that observed in silk and other biological materials (Iguchi et al., 2000). In a similar manner, both the traction and separation models can be used to estimate mechanical properties for these interfaces including the interlayer shear modulus and Young's modulus. Using composite theories such as the shear-lag model (Liu et al., 2012; Liu and Xu, 2014; Wei et al., 2012), one can predict the mechanical performance of CNC thin films based on the interlayer shear modulus, G and Young's modulus of the CNCs, E . The models developed for the traction potentials are particularly useful as they can be used to obtain values of G as shown in Figure 7A. Using experimentally reported values of the elastic modulus of CNCs in literature (Moon et al., 2011), the shear-lag model (Liu et al., 2012; Liu and Xu, 2014; Wei et al., 2012) can be employed to estimate the effective elastic modulus, E_{eff} , of a CNC thin film.

Figure 7: (A) Stress-strain plot for the shearing of two CNC crystals based on the traction potential developed in Eq. (9). The interlayer shear modulus is estimated by taking the initial slope of the stress-strain curve and the strain at failure initiation is taken as the strain at the maximum stress. (B) Illustration of a CNC neat film where each of the green rectangles represents a CNC crystal. A shear-lag model is used to predict the overall performance of this system based on the dimensions and mechanical properties of the crystal and the interfacial shear properties obtained from stress-strain plots shown in panel (A).

Using specific values of the interlayer shear modulus as reported in the SI, an effective elastic modulus can be estimated for an aligned, CNC thin film as illustrated in Figure 7B. Depending on the orientation of the CNCs (axial vs. transverse) and dominate interface ((110) vs. (200)), the shear-lag model estimates the effective modulus of these films to range from 0.8 - 63 GPa. When comparing these values to those reported in literature for bacterial cellulose (10 – 20 GPa)(Iguchi et al., 2000) and aligned, wood-based (7 – 30 GPa)(Reising et al., 2012) CNC films, it is observed that the predictions are in good agreement with experimentally obtained values (see Table S3 in Supplemental Information for comparison). However, factors such as crystal misalignment, surface defects on CNCs due to processing conditions, and presence of amorphous domains are not taken into account in these predictions – all of which would alter the predicted values of the effective modulus. These factors would be important to consider in developing more advanced models and accurate predictions for the performance of CNC films. However, this simple model illustrates that knowledge about the interfacial behavior between CNC surfaces coupled with knowledge of failure planes within the crystals(Sinko et al., 2014) is central to developing an enhanced understanding of CNC neat films.

Further, the adhesion energy calculations performed here can be repeated for polymer-CNC interfaces in order to develop coarse-grained (CG) models(Hsu et al., 2014) of CNC-polymer interactions. Even though polymers may modify CNC surfaces (i.e. polymer grafting, changing surface conformation, etc.), the underlying van der Waals interactions and hydrogen bonding should remain the dominant forces at interfaces. These CG models will improve computational efficiency of molecular simulations and will open the door for studying new polymer-CNC bionanocomposites. Specifically, these CG models can be used to simulate the effect of CNCs within these bionanocomposites due to the development of interphase regions that have a

pronounced effect on properties such as the glass-transition temperature and elastic modulus(Dong et al., 2012; Xia et al., 2014). These efforts will allow for an enhanced materials-by-design approach for CNC hierarchical materials that will help to improve upon the current shortcomings in the performance of these materials. Beyond CNCs, these results could be extended to describe interface within other highly ordered, aligned material systems such as actin networks(Kang et al., 2011) in muscle or multi-layered graphene sheets(Ruiz et al., 2015).

4. Conclusions

Our analyses on the interfaces between cellulose nanocrystals based on simulation and theory have revealed unique insight into these interfaces. We have discovered that the interfaces are governed by both weak secondary interactions and extensive hydrogen bonding that lead to impressive adhesion between fibrils exceed that of many common engineering materials. Beyond fundamentally understanding the molecular mechanisms that provide strength to these interfaces, we have been able to mathematically describe the energy landscape using models that are physically informed by both the geometry of the fibril surfaces and dominant interaction mechanism at the interface.

Separation simulations have revealed that surfaces exhibiting hydrogen bonding are significantly stronger than those that do not, while van der Waals interactions are important for all surfaces. Shearing simulations illustrated that there is a pronounced transition from continuous sliding behavior for hydrogen bond-dominated surfaces to stick-slip behavior for van der Waals surfaces as a result of the specific surface chemistry. Using these observations, analytical models were developed that describe that shape of the energy landscapes for these different processes. The separation model was inspired by the simple separation of van der Waals surfaces and was shown to be applicable for any surface with underlying van der Waals

interaction. The shear landscape was developed based on a combination of the Prandtl-Tomlinson model for atomic friction and scaling relations for separation of van der Waals surfaces. These mathematical descriptions are the most important contribution of this study, as they provide a way to upscale key information about CNC-CNC interfaces to link simulations to experimental data and observations. Although the models developed and parameters reported are for non-functionalized, “perfect” CNCs, our models could easily be extended to functionalized CNC surfaces by adjusting the fitting constants based on the specific type and density of the functional group – again demonstrating the versatility and fundamental nature of this generalized model.

The results of this work will help benefit the efforts to develop hierarchical materials that leverage tunable interfaces that can be used to control a number of material properties. Atomistic modeling efforts have helped to achieve impressive mechanical properties in metals by looking at polycrystallinity, grain boundary physics, dislocations and other mechanisms. The result of the current work falls along the same lines and utilizes the same principles while focusing on polysaccharide nanocrystals and the materials made thereof. Extending this work to other biological and synthetic interfaces will provide guidance towards the development of new functional materials that follow natural evolutionary design characteristics and principles.

ASSOCIATED CONTENT

Supporting Information. Supporting information including simulation protocols and fracture surface energy calculations are provided.

Author Contributions

The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

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