



A continuum-based structural modeling approach for cellulose nanocrystals (CNCs)

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ABSTRACT

We present a continuum-based structural model to study the mechanical behavior of cellulose nanocrystals (CNCs), and analyze the effect of bonded and non-bonded interactions on the mechanical properties under various loading conditions. In particular, this model assumes the uncoupling between the bonded and non-bonded interactions and their behavior is obtained from atomistic simulations. Our results indicate that the major contribution to the tensile and bending stiffness is mainly due to the cellulose chain stiffness, and the shear behavior is mainly governed by Van der Waals (VdW) forces. In addition, we report a negligible torsional stiffness, which may explain the CNC tendency to easily twist under very small or nonexistent torques. In addition, the sensitivity of geometrical imperfection on the mechanical properties using an analytical model of the CNC structure was investigated. Our results indicate that the presence of imperfections have a small influence on the majority of the elastic properties. Finally, it is shown that a simple homogeneous and orthotropic representation of a CNC under bending underestimates the contribution of non-bonded interaction leading up to 60% error in the calculation of the bending stiffness of CNCs. On the other hand, the proposed model can lead to more accurate predictions of the elastic behavior of CNCs. This is the first step toward the development of a more efficient model that can be used to model the inelastic behavior of single and multiple CNCs.

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1. Introduction

Nature has evolved efficient strategies to make materials with hierarchical internal structure that often exhibit exceptional mechanical properties. One such example is found in cellulose, which has achieved a high order of functionality and mechanical properties through a hierarchical structure with an exceptional control from the atomic level all the way to the macroscopic level. Cellulose is present in a wide variety of living species (trees, plants, algae, bacteria, tunicates), and provides the base reinforcement structure used by organisms for high mechanical strength, high strength-to-weight ratio, and high toughness. Additionally, being the most abundant organic substance on earth, cellulose has been used by our society as an engineering material for thousands of years, and are prolific within our society, as demonstrated by the enormity of the world-wide industries in cellulose derivatives, paper/packaging, textiles, and forest products.

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More recently, a new class of cellulose base particles are being extracted from plants/trees, cellulose nanocrystals (CNCs), which are spindle-shaped nano-sized particles (3–20 nm in width and 50–500 nm in length) that are distinct from the more traditional cellulose materials currently used (e.g. molecular cellulose and wood pulp) (Habibi et al., 2010; Moon et al., 2011a; Moon et al., 2016). It should be mentioned that CNCs are different from the crystalline cellulose domains that can be found in pulp. CNCs are larger in size and contain a mixture of crystalline and disordered structure, they have surfaces and they can be considered as individual particles. As a result, CNCs offer a new combination of particle morphology, properties and chemical functionalities that enable CNCs for use in applications that were once thought impossible for cellulosic materials. CNCs have shown utility in many engineering applications (Mariano et al., 2014; Moon et al., 2016; Grishkewich et al., 2017), for example, biomedical (Klemm et al., 2011; Lin and Dufresne, 2014), nanocomposites (Huq et al., 2012; Miao and Hamad, 2013; Mariano et al., 2014; Yang et al., 2014), barrier/separation membranes (Carpenter et al., 2015), and cementitious materials (Cao et al., 2015; Cao et al., 2016a, 2016b).

To gain greater insight as to how best use CNCs in various engineering application areas, a comprehensive understanding of the mechanics of CNCs is needed. The characterization of the mechanical properties of nanomaterials via experimental testing has always been challenging due to their small size (Sakurada et al., 1962; Sakurada et al., 1964; Li and Chou, 2003; Rusli and Eichhorn, 2008; Lahiji et al., 2010; Wagner et al., 2011; Pakzad et al., 2011), resulting in large uncertainties related to testing near sensitivity limits of a given technique, the same is true when characterizing CNCs (Wagner et al., 2011). For CNCs, to help offset limitations in experimental testing, numerical modeling has been useful in predicting the mechanical properties of crystalline cellulose. Besides thermo-elastic property predictions (Moon et al., 2011a; Dri et al., 2013; Dri et al., 2014; Dri et al., 2015), recently, it was shown that the dimensions of CNC particles are optimized for fracture energy and surface area-to-volume ratio (Sinko et al., 2014). In addition, interfacial study of CNC particles reveals that the contribution of both VdW interactions and hydrogen bonding responsible for the adhesion strength between CNCs (Sinko and Keten, 2015). Sinko and Keten also studied the shear and tensile failure of the interfaces between CNCs and proposed analytical model to describe their energy landscapes (Sinko and Keten, 2015). These examples demonstrate the utility of numerical modeling of gaining insight about the mechanisms that influence the mechanical behavior of CNCs.

Modeling approaches devoted to the prediction of the mechanical performance of nanomaterials can be divided into two major groups (i) atomistic, and (ii) continuum mechanics (Yakobson et al., 1996; Arroyo and Belytschko, 2002; Li and Chou, 2003; Arroyo and Belytschko, 2004; Cao and Chen, 2006; Jiang et al., 2006; Buehler, 2008; Sauer and Wriggers, 2009; Scarpa et al., 2009; Arash and Wang, 2014). Although atomistic approaches are a more appropriate in most cases for nano-scale simulations, they are very inefficient for large macromolecules or time span (Jiang et al., 2006; Li and Chou, 2003; Scarpa et al., 2009). Molecular dynamics (MD) solves the equation of motion for a large system of particles. The accuracy of MD simulations highly depends on appropriate choice of the force field (FF) that represents the interaction between the atoms (Matthews et al., 2012; Dri et al., 2015). FFs represent a set of mathematical functions, including their specific parameters, employed to describe the different bonded, e.g. covalent bonds, and non-bonded, e.g. hydrogen bonds and VdW forces, atomistic interactions in order to predict certain material properties. As more computer power has become available over the years, more sophisticated mathematical functions have been developed and employed to improve predictions. For instance, reactive force fields, such as ReaxFF (Van Duin et al., 2001), which are based on bond length/order relationship, were developed and utilized intensely for various types of materials, mainly due to their ability to simulate bond forming and breaking, which is necessary for many mechanical investigations (Van Duin et al., 2001; T van Duin et al., 2003; Buehler, 2006; Chenoweth et al., 2008; Mattsson et al., 2010; Rahaman et al., 2011). These reactive force fields are also expected to be more accurate than classical non-reactive force fields, and closer to those predictions obtained with First principles density functional theory (QM-DFT) (Van Duin et al., 2001; Mattsson et al., 2010; Rahaman et al., 2011; Chenoweth et al., 2008; van Duin et al., 2003; Buehler, 2006). In particular, ReaxFF has an explicit hydrogen bond (*h*-bond) term that allows us to individually study its effect on the mechanical properties.

Indeed, both QM-DFT and MD have been used to predict the mechanical behavior of CNCs. Recently, (Dri et al., 2013; Dri et al., 2014) employed QM-DFT with a semi-empirical correction for (VdW) interactions to reveal that the elastic properties of crystalline cellulose exhibits extreme anisotropy due to different type of dominant interactions, e.g. covalent, VdW and *h*-bond in different planes, for a wide range of temperatures. However, even for simple elastic properties, the competing contribution between bonded and non-bonded interactions remains to be studied in detail. MD has been undoubtedly the most predominant predictive tool for CNCs in the last few years (Kroon-Batenburg and Kroon, 1997; Neyertz et al., 2000; Eichhorn and Davies, 2006; Tanaka and Iwata, 2006; Bergenstrale et al., 2007). In particular, ReaxFF parameters have already been studied for CNCs (Wu et al., 2014; Dri et al., 2015) and compared with *ab initio* calculations for both conformational and mechanical analysis (Wu et al., 2014). In this paper, we employ the ReaxFF parameters proposed by (Chenoweth et al., 2008) due to its superior performance on Young's modulus and lattice parameters of CNC among other ReaxFF parameters (Dri et al., 2015).

In contrast, continuum mechanics approaches are suitable to model large sized systems or time scale (Li and Chou, 2003; Buehler, 2008). However, turning a complex atomistic model into a simplified continuum or structural representation requires understanding of the governing mechanisms and physics at atomistic scale, which can be attained with atomistic modeling such as MD. In particular, continuum and structural mechanics have been used to model carbon nanotube and graphene in the past years following finite element frameworks (Yakobson et al., 1996; Arroyo and Belytschko, 2002; Li and Chou, 2003; Arroyo and Belytschko, 2004; Cao and Chen, 2006; Jiang et al., 2006; Scarpa et al., 2009; Lin et al., 2011; Arash and Wang, 2014). In these studies, either each individual covalent bond is modeled as a beam element (Li and Chou, 2003;

Scarpa et al., 2009) or a group of atoms is simplified following a shell element formulation (Yakobson et al., 1996; Cao and Chen, 2006). However, the most important challenge for continuum models is to capture the non-local nature of interactions at nano-scale, e.g. VdW forces. For instance, non-local continuum theories were applied to the case of beam, plate and shell in the past (Arash and Wang, 2014). In some studies nonlinear springs based on Lennard–Jones (LJ) model were employed between each individual atoms to model VdW forces (Li and Chou, 2003). Deriving Constitutive cohesive equations for VdW forces based on LJ potential were also proposed by (Jiang et al., 2006). A finite element model (FEM) for nano-scale contact problems based on potential was proposed by (Sauer and Wriggers, 2009).

In this work, we present a continuum-based structural model that uncouples bonded and non-bonded interactions and substitutes them with an equivalent interaction model. The model is implemented under a finite element (FEM) framework, and it allows us to better quantify the effect of bonded and non-bonded interactions on the overall elastic behavior of CNCs under various loading conditions, including axial loads, bending, torsion and shear. Understanding the role of different interactions on each mechanical loading helps to (i) understand the source of elastic anisotropy in CNC and (ii) develop a more simplified mathematical model later on, FEM or coarse graining models, for mechanical properties of CNC. Ancillary atomistic simulations are employed to (i) inform the continuum model and (ii) verify some key results. The main focus of this study is on the properties of a single CNC molecule as opposed to many CNCs. However, we expect future work to focus on the characterization of the surface properties and their incorporation in the model, enabling the modeling large system with many CNC particles (Sinko and Keten, 2015; Qin et al., 2017).

2. Structure of CNCs

Cellulose is a linear chain of 1–4 linked β -D-glucopyranose and during the biosynthesis process, cellulose chains bundle together in highly ordered parallel stacking, forming crystalline regions (cellulose I) that have two distinct polymorphs called cellulose I α and I β . Cellulose I β is the more stable phase, dominant in plants and the focus of this study (Jarvis, 2003; Klemm et al., 2005; Quesada Cabrera et al., 2011). X-ray neutron diffraction studies concluded that Cellulose I β contains two cellulose chains in a monoclinic unit cells with different inter-chains *h*-bonding systems which can be distinguished by the so-called A and B *h*-bonding patterns (Nishiyama et al., 2002). We focus on cellulose I β with network A as the most commonly occurring polymorphs in higher plant cell wall (Moon et al., 2011b). Figure 1a shows a schematics of an idealized CNC extracted from plants/trees, and is within the range of predicted CNC geometries having an estimated width of 2–3.5 nm, consisting of 18–36 chains and different proposed cross-sectional shapes (e.g. diamond, square or hexagonal) (Bergenstrale et al., 2007; Moon et al., 2011b; Zhao et al., 2013).

The lattice parameters for cellulose have been experimentally measured by several authors (Nishiyama et al., 2002; Wada et al., 2004; Langan et al., 2005; Nishiyama et al., 2008), using different experimental techniques. For instance, for the cellulose I β with a network A structure, these unit cell values were reported (Nishiyama et al., 2002) to have the following values: $a = 7.784 \text{ \AA}$, $b = 8.201 \text{ \AA}$, $c = 10.380 \text{ \AA}$, $\alpha = 90^\circ$, $\beta = 90^\circ$, $\gamma = 96.55^\circ$, with a $658.3 \text{ \AA}^3$ volume at 293 K (Fig. 1(b)–(c)). Cellulose I β has P21 symmetry and the layers are displaced along the *c*-axis alternatively by $+c/4$ and $-c/4$ forming the so-called center and origin chains respectively (Fig. 1(b)). Intra- and inter-chain *h*-bonds are shown in Fig. 1(d) based on the *h*-bond pattern A. The inter-chain *h*-bonding is dominant within the (200) plane, also known as “*h*-bonded” plane. A schematics of the hydrogen bond is included in Fig. 1(e). On the other hand, VdW forces are believed to contribute to the bonding within planes (110) and ($\bar{1}\bar{1}0$) with a lesser influence of the *h*-bonds.

3. Methodology

3.1. Continuum-based structural model

The FF potentials typically used in MD and MM to account for the interaction between atoms are categorized into bonded and non-bonded terms (Tanaka and Iwata, 2006). In the proposed continuum-based structural model (or simply *continuum model*, CM), we follow a similar approach, and we assume that the bonded (i.e., covalent bonds) and non-bonded interaction (*h*-bonds and VdW forces) can also be decoupled. Previous works have shown that *h*-bonding and VdW interactions are the primary non-bonded interactions in CNC (Nishiyama et al., 2002; Kong and Eichhorn, 2005; Lindman et al., 2010; Sinko and Keten, 2015). While most atomistic models of CNC using classical FF describe the *h*-bonds as electrostatic interactions (Sinko and Keten, 2015), ReaxFF allows us to consider the *h*-bonding explicitly. Therefore, although other non-bonded terms are present in a FF (e.g. electrostatic term), their effects will be implicitly considered as a part of the VdW forces or covalent bond, for intra-chain and inter-chain interaction respectively. As such, the model consists of three main dominant interactions: the elastic behavior of the individual chain, the interaction of the chains on an *h*-bonded plane, and the interaction between *h*-bonded planes.

The individual chains are considered to behave linearly elastic under infinitesimal strains. Additionally, due to their small thickness, the chains are assumed to undergo axial, torsional and bending deformation. As such, they are modeled as elastic beams. In a finite element framework, each chain is discretized with 3D Euler–Bernoulli (Fish and Belytschko, 2007) beam elements passing through the center of mass of the chain. Further analysis will validate these assumptions. A schematics of a beam element replacing two cellulose rings along a chain is shown in Fig. 2(a) and (b) in blue. The beams main elastic characteristics, which include tension stiffness, *EA*, bending stiffness, *EI* and torsional stiffness, *JG*, are obtained from

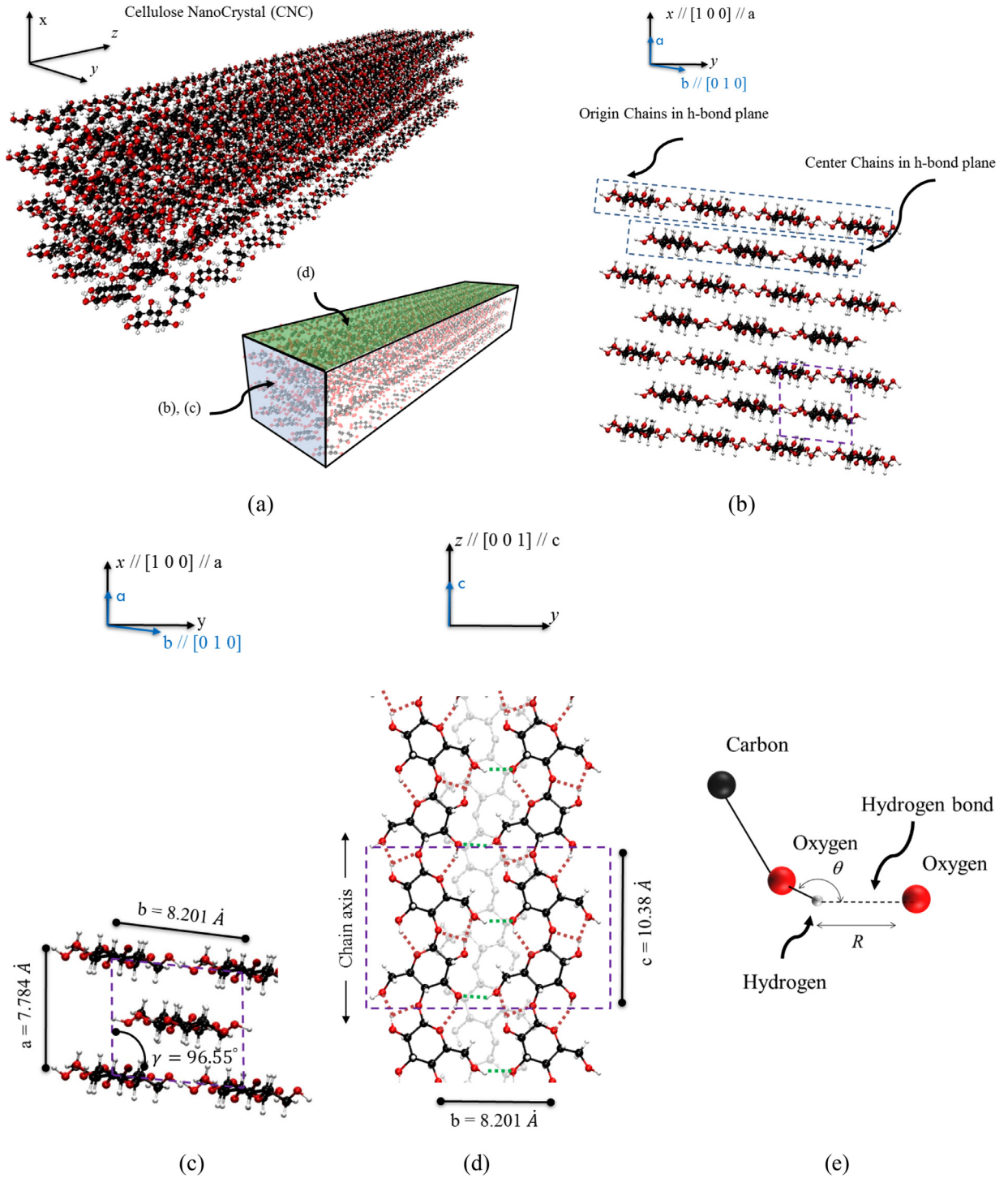


Fig. 1. Atomistic structure of CNC (Nishiyama et al., 2002). Red spheres denote oxygen ions, gray spheres represent carbon ions and white spheres represent hydrogen ions. (a) 3D view, (b) CNC 3×3 (square) structure is used in this work. The origin and center chains in *h*-bond plane (c) Unit cell of CNC in *x*-*y* coordinate (d) View along the *c*-axis direction. The intra- and inter-chain *h*-bonds are shown in blue and green dash lines, respectively. Note that only a fraction of the total length is being showed. (e) *h*-bond energy depends on distance and angle between donor and acceptor as shown as R and θ respectively. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article).

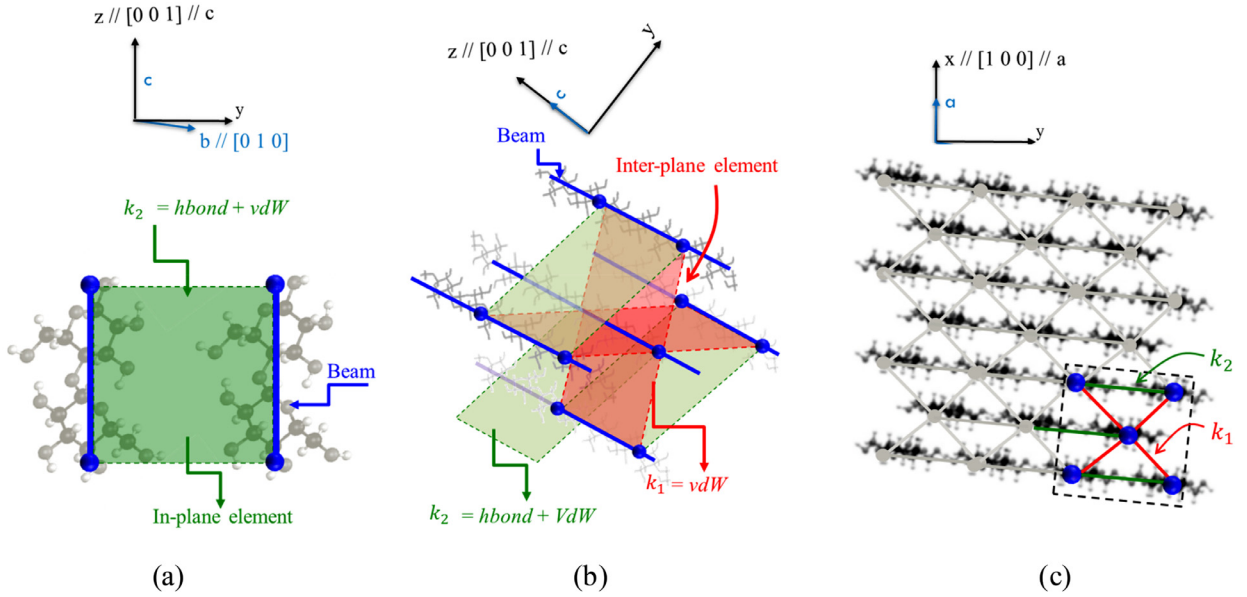


Fig. 2. Schematics of the transition from atomistic to continuum by replacing chains with beams, in-plane non-bonded interactions (h -bond and VdW) with in-plane surface and inter-plane non-bonded interactions with Inter-plane surface. (a) Representation of beams and in-plane surface replacing chains and in-plane non-bonded interactions (h -bond and VdW). The small blue spheres represent the beam element nodes (b) 3D representation of continuum model for beam, in-plane and inter-plane surfaces. (c). The cross-section of the 3×3 CNC with intra-plane and inter-plane surfaces shown in green and red colors with k_2 and k_1 as their stiffness respectively. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article).

atomistic simulation of a single isolated CNC chain. The elastic properties of each chain include the contribution of the covalent bonds, intra-chain h -bond and VdW forces between atoms inside a chain. While the schematic representation in Fig. 2(a) and (b) depicts a beam element representing two glucose rings, the number of rings being represented by each element may be varied. A mesh sensitivity analysis addressing this point was carried out and included in Appendix A4.

The h -bond and VdW interaction between chains lying on the h -bonded plane is modeled with special springs elements, intra-plane element, distributed along the chain direction as shown in Fig. 2 with green color. In addition, inter-plane elements are developed to connect the first neighbor chains for inter-plane interactions, only VdW interactions, as shown in Fig. 2 with red colors.

Van der Waals forces are typically modeled by the Lennard–Jones (LJ) potential in MD simulations, when the distance between any two atoms is less than cutoff distance. While previous works have considered these types of non-local interactions in continuum models (Sauer and Wriggers, 2009; Arash and Wang, 2014), in this work we consider that only the nearest neighbor chains interact through VdW forces as shown in Fig. 2. Considering the unit cell dimension in $[0\ 1\ 0]$ and $[1\ 0\ 0]$ directions, $b = 8.201\text{ \AA}$ and $a = 7.784\text{ \AA}$, respectively, the second nearest neighbor distance in $[0\ 1\ 0]$ direction, $12\text{ \AA}$, is much larger than LJ equilibrium distance, σ , for C, O and H atoms, $\cong 6\sigma$, therefore there is almost no VdW interaction between second neighbor in $[0\ 1\ 0]$ direction (less than 0.01% of the well depth). For $[1\ 0\ 0]$ direction the second nearest neighbor distance is $7.784\text{ \AA}$, which is still large enough, $\cong 4\sigma$, to be neglected (less than 0.1% of the well depth). We should also mention that the primary electrostatic interactions for CNC is hydrogen bonding (Nishiyama et al., 2002; Kong and Eichhorn, 2005; Lindman et al., 2010; Sinko and Keten, 2015), which has short-range effect and is modeled explicitly as h -bond. For systems such as ionic solids, where long-range interactions are important, the first nearest neighbor assumption will need be evaluated and replaced with a more sophisticated model (Marshall and Dayal, 2014). The overall effect of VdW forces between two nearest chains is applied on the beam elements passing through the center of mass of the chains (Fig. 2). The constitutive equation for VdW element is similar to the h -bond element except that these elements connect the neighbor chains at different planes.

The finite element formulation is obtained from the principle of virtual work, which can be expressed as follows:

$$\int_V (b_i - \rho \ddot{u}_i) \delta u_i dV + \int_{\partial V} t_i \delta u_i d\Gamma = \int_V S_{ij} \delta \varepsilon_{ij} dV + \int_{\Gamma} R_{ij} T_{ij} (\delta u_i^+ - \delta u_i^-) d\Gamma \quad (1)$$

Where b is body forces on volume V , ρ is density, $\ddot{u}$ is acceleration, t is boundary tractions on ∂V , u is displacement, S is second Piola–Kirchhoff stress tensor ε is Green–Lagrange strain tensor, R local to global transformation matrix and u^+/u^- are displacement jumps between donor and acceptor when T is their traction forces in h -bond element. After discretization, and in the absence of body force, Eq. (1) can be solved with a time integration solver as follows.

$$M\ddot{u} = F_{\text{ext}} - F_{\text{int}} \quad (2)$$

Where $\mathbf{M}$, F_{ext} and F_{int} are lump mass matrix, external and internal force vectors respectively. The explicit method is adopted to handle potential instabilities. For simplicity, the constitutive relations for traction-separation of h -bond and VdW forces are initially based on linear elastic response and are defined as:

$$T_i^h = K^h \delta_{ij} \Delta_j^h \quad (3)$$

$$T_i^v = K^v \delta_{ij} \Delta_j^v \quad (4)$$

Where T_i^h and T_i^v are traction forces, K^h and K^v are stiffness and Δ_j^h and Δ_j^v displacement jumps for h -bond and VdW elements respectively and δ_{ij} is Kronecker delta function. Although the actual response of VdW and h -bond potentials are nonlinear, here we use instantaneous stiffness for the structure at equilibrium and limit our simulations to small deformations. Extension to nonlinear relationships based on LJ potentials can easily be implemented under the same framework and will be presented in future work.

3.2. Determination of the main parameters

3.2.1. Cellulose chain mechanical properties

We carried out ancillary molecular mechanics (MM) simulations on a single cellulose chain to obtain the main mechanical properties needed for the continuum model. As the deformation of cellulose chains inside the CNC is mostly restricted by their interaction with neighboring chains, MD simulations of unconstrained single chains may not be a good option. In MM simulations, the specific deformation (e.g. bending), is prescribed uniformly to all atom and energy minimization is used to find a stable structure with minimum total potential energy. In particular, we extract the axial, bending, torsion and shear properties through specific tests such as simple tension, bending and torsion thought experiments. These MM simulations are done on single chains with different lengths using LAMMPS (Plimpton et al., 2007) with a ReaxFF force field and Hessian-free truncated Newton (hftn) algorithm for energy minimization (Plimpton et al., 2007). For each mechanical tests appropriate displacement is applied to all atoms in the chain and after energy-minimization the corresponding stiffness is obtained by relating total potential energy to stored strain energy in mechanics of solids (Li and Chou, 2003).

$$\frac{U_A}{L} = 0.5EA\epsilon^2, \quad \frac{U_M}{L} = 0.5EI\kappa^2, \quad \frac{U_T}{L} = 0.5GJ\kappa^2 \quad (5)$$

Where U_A , U_M and U_T are potential energy for tension, bending and torsion respectively and EA , EI and GJ are stiffness for tension, bending and torsion respectively, δ is displacement, κ is curvature and L is the length of the chain. The results of these simulations are shown in Fig. 3(a)–(c). Assuming small strains problem, EA , EI and GJ can be obtained by parabolic data fitting of $U_A/L - \epsilon$, $U_M/L - \kappa$ and $U_T/L - \kappa$ curves, respectively. According to the results, the parabolic equation for tension is $U_A/L = 15.5(nN) \epsilon^2 - 0.0186(nN) \epsilon + 1E - 4(nN)$, for bending is $U_M/L = -2.5(nN.nm^2) \kappa^2 + 0.8355(nN.nm) \kappa + 1E - 4(nN)$ and for torsion is $U_T/L = 0.8334(nN.nm^2) \kappa^2 + 0.0856(nN.nm) \kappa - 8E - 5(nN)$. Based on the obtained parabolic equations and Eq. (5), the average stiffness values used in our continuum model are as follow:

$$EA = 31 \pm 2 \text{ nN}, \quad EI = 5.0 \pm 2 \text{ nN.nm}^2, \quad GJ = 1.5 \pm 0.5 \text{ nN.nm}^2 \quad (6)$$

Where EA , EI and GJ are tension, bending and torsion stiffness of a single chain. As it can be inferred from the MM analysis suggest that the bending and torsional stiffness for single chain can be negligible in comparison with the axial stiffness.

3.2.2. h -bond properties

As previously discussed, ReaxFF has an explicit h -bond term that allows us to individually study its effect on the mechanical properties. To obtain h -bond properties for our continuum model the potential energy contribution for each h -bond in ReaxFF (Van Duin et al., 2001), which is defined as below, is employed.

$$U_{H-Bond} = P_{hb1} \times (1 - e^{-P_{hb2} \times BO}) \times e^{-P_{hb3} \times \left(\frac{R_0}{R} + \frac{R}{R_0} - 2\right)} \times \sin^4\left(\frac{\theta}{2}\right) \quad (7)$$

Parameters P_{hb1} , P_{hb2} , P_{hb3} and R_0 are exclusive parameterization used in each ReaxFF force field whereas BO, Bond Order, R, distance between donor and acceptor, and θ , h -bond angle, depend upon the geometry configuration.

The second derivative of the potential energy with respect to the interatomic distance between donor and acceptor (R) provides the stiffness of the h -bond, which is the main parameter for h -bond element in our continuum model.

$$K_{R-HBond} = P_{hb1} \times (1 - e^{-P_{hb2} \times BO}) \times \sin^4\left(\frac{\theta}{2}\right) \times \left[P_{hb3}^2 \times \left(-\frac{R_0}{R^2} + \frac{1}{R_0}\right)^2 - P_{hb3} \left(\frac{2R_0}{R^3}\right) \right] \times e^{-P_{hb3} \times \left(\frac{R_0}{R} + \frac{R}{R_0} - 2\right)} \quad (8)$$

Note that, since the variation of h -bond angle is small for infinitesimal deformations and the value for $K_{\theta-Hbond}$ is much smaller than $K_{R-Hbond}$, only derivation with respect to R is explicitly considered in the model. Fig. 4 represents the stiffness values for h -bond obtained based on Eq. (8). However, the h -bond stiffness in our model (Fig. 2.(a)) is defined as a set of distributed forces over the element length. To overcome this problem, we approximate the contribution of the h -bonds

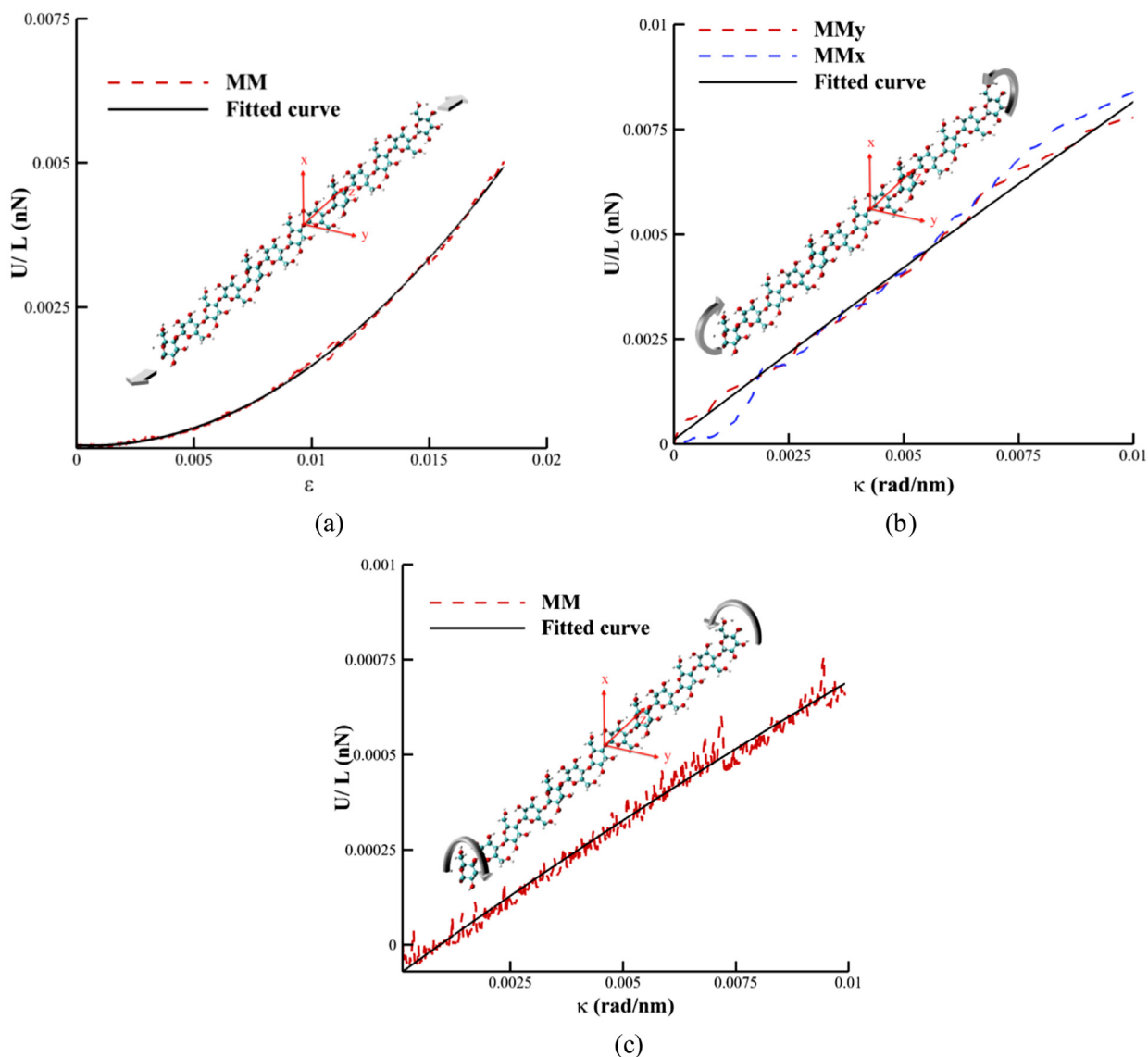


Fig. 3. Finding the mechanical properties of a single chain from MM (a) simple tension test on a single chain (b) Applying torsion displacement to a single chain (c) Applying two bending displacement around x and y axis on a single chain.

with an average stiffness value. There are two main inter-chain h -bonds per each cellulose ring with the values of 4.5 and 1.5 Kcal/mole $\text{\AA}^2$ as shown in Fig. 4.(b). Therefore, by dividing the value of overall local stiffness of h -bond, 6 Kcal/mole $\text{\AA}^2$, by the length of a ring, 5.19 $\text{\AA}$, the average stiffness value is obtained as 1.156 Kcal/mole $\text{\AA}^3$ (8 nN/nm²).

3.2.3. Stiffness of VdW element

To be able to find the stiffness of VdW element in normal and shear direction, MD analysis at 1 K has been done on two chains with different length (Fig. 5). Note that the equilibrium distance of two chains in crystalline cellulose is different from the equilibrium distance of two isolated chains due to the presence of other chains in a crystal. Therefore, at the beginning, two chains are placed at the equilibrium distance of two chains in a crystal, 8.201 $\text{\AA}$ and 5.57 $\text{\AA}$ for center to center distance of in-plane and inter-plane chains respectively, and the position of the leftmost oxygen atoms in the left chain and rightmost oxygen atoms in the right chain are fixed during equilibrium. To ensure that only the VdW interactions are contributing in our calculations, the h -bond cut off distance is set to zero. Moving a chain in the normal and tangential direction while keeping the other chain fixed (at the leftmost oxygen atoms) and calculating the total force-displacement relationship, the VdW behavior and consequently stiffness in normal/tangential direction is obtained. The analysis was done for both intra-plane and inter-plane VdW interactions (shown in red and green colors respectively in Fig. 2) to increase the

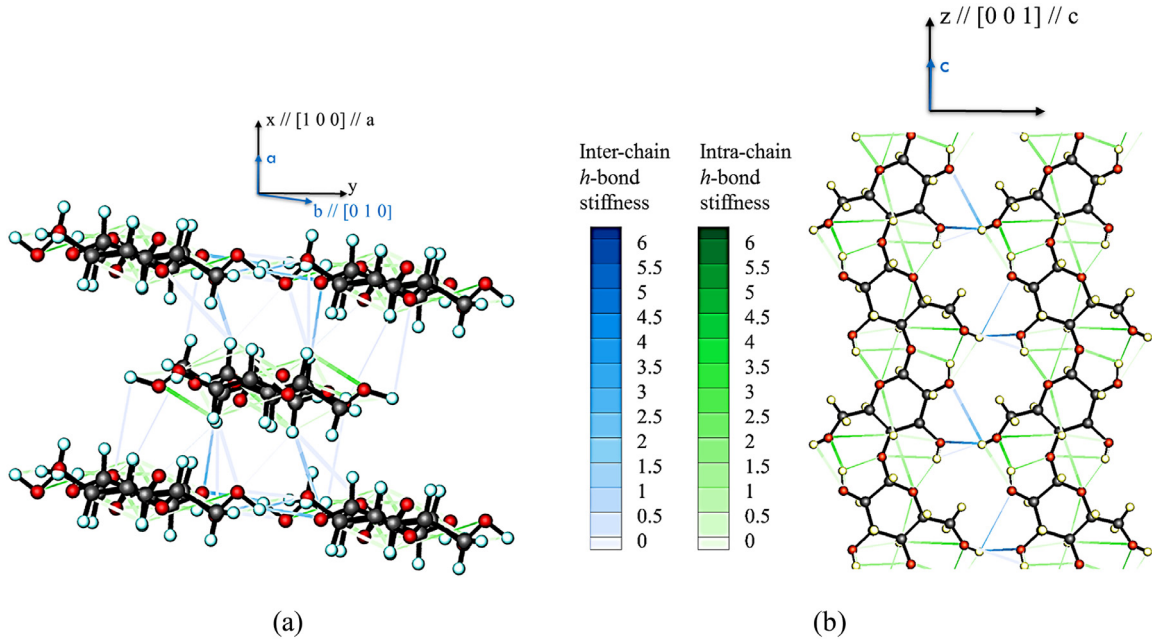


Fig. 4. h -bond stiffness (represented as blue and green contour for inter-chain and intra-chain h -bonds respectively) for the unit cell of CNC structure. Stiffness values are in Kcal/mole Å². (a) Reduced view along the a -axis (b) View along the c -axis (perpendicular to the page). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article).

accuracy of the model. It is worth to mention that here MD simulation is used over MM in order to have control on distance of two chains and to overcome local minimum potential energy barrier during separation.

Fig. 5 represents the MD results for the normal (Fig. 5(b) and (d)) and tangential (Fig. 5(a) and (c)) directions for both intra-plane (Fig. 5(a) and (b)) and inter-plane (Fig. 5(c) and (d)) chains. The analysis was done for chains with different degree of polymerization (DP represents the number of monomeric units in a cellulose chain) 12, 24 and 48 to understand the effect of chain length on the results. Although the force-displacement relationship in both normal and tangential directions is nonlinear, our results in Fig. 5(a) and (c) suggest that force-displacement behavior can be assumed linear for infinitesimal deformations (i.e., 5% strain) around the equilibrium point. For the VdW stiffness in the normal direction, the stiffness at equilibrium distance of two chains in the crystal (not the equilibrium distance of two isolated chains) has been used to reduce the error associated with the nonlinearity of VdW forces in the normal direction (dashed black line in Fig. 5).

The non-bonded stiffness values used in our continuum model for inter- and intra-plane element are given by the following expressions:

$$K_{1n} = 7.0 \pm 2.0 \frac{nN}{nm^2}, \quad K_{1t} = 1.7 \pm 0.3 \frac{nN}{nm^2} \quad (9)$$

$$K_{2n} = 14.0 \pm 2.0 \frac{nN}{nm^2}, \quad K_{2t} = 2.5 \pm 0.5 \frac{nN}{nm^2} \quad (10)$$

where K_{1n} and K_{1t} are the inter-plane non-bonded stiffness in normal and tangential direction, respectively; while K_{2n} and K_{2t} are the in-plane non-bonded stiffness in normal and tangential direction, respectively. Note that K_{2n} in Eq. (10) also includes 8 nN/nm² for the h -bond stiffness.

4. Numerical Results

The proposed continuum-based structural model (denoted as CM), along with the MD simulations, is employed to study the effect of bonded and non-bonded interactions of CNCs in tension, shear, bending and torsion. The fact that bonded and non-bonded interactions are separated in the continuum model allows us to understand the contribution of each term on the overall response by direct comparisons with MD at 1 K. Although both MD at 1 K and MM may be seem similar, overcoming potential barriers under certain loading conditions is only possible with MD simulations. Using MD simulations at 1 K has also been used by many authors before (Cao and Chen, 2006; Chang and Hou, 2006; Chang, 2013) to eliminate the effect of thermal fluctuations on the mechanical properties. In addition, DFT calculations shows that temperature (0–500 K) has little effect on the mechanical properties of the CNC (Dri et al., 2014). Since the mechanical tests in MD are performed after minimization and equilibration, the equilibrated structure of CNC has been used for obtaining the geometrical properties of the continuum model such as the center of mass for each chain and average position of donors and acceptors. In all these

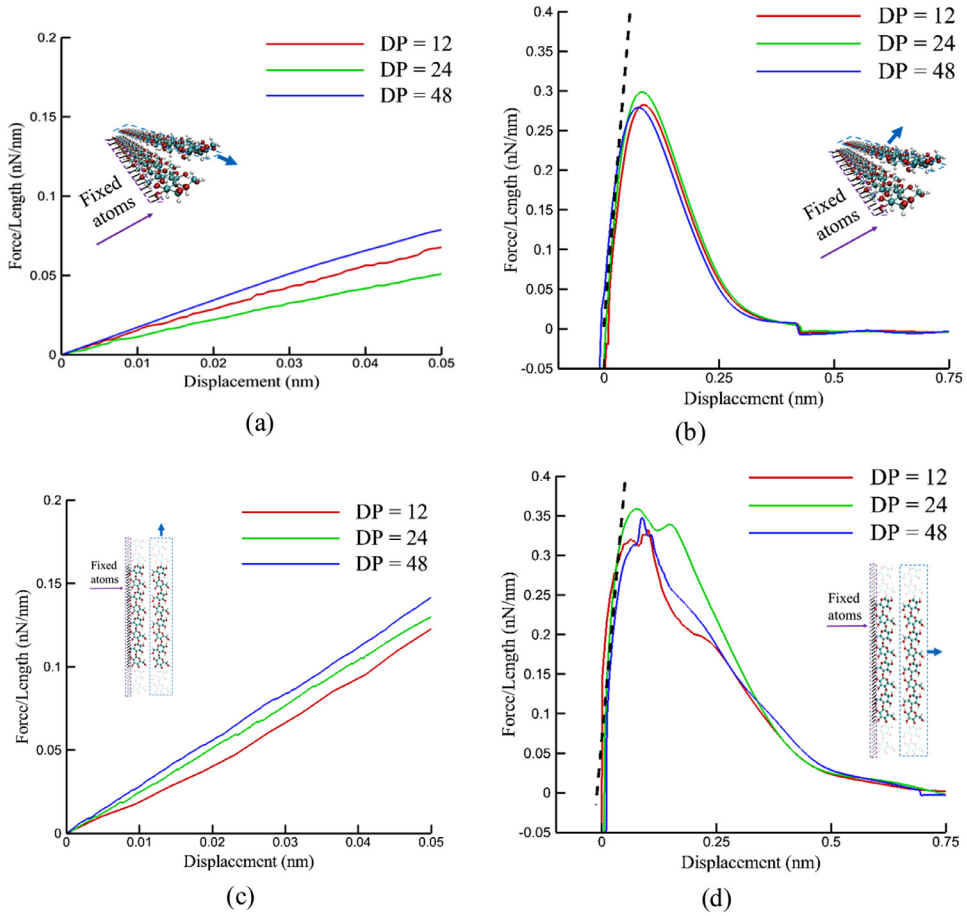


Fig. 5. Force per length-displacement curves for VdW forces between two Chains with different lengths. (a) Tangential force-displacement response for inter-plane VdW forces (b) Normal force-displacement response for inter-plane VdW forces (c) Tangential force-displacement response for in-plane VdW forces (d) Normal force-displacement response for in-plane VdW forces.

cases, MD analysis is performed on a 3×3 square CNC with $DP=24$ using ReaxFF with time step 0.5 fs. First, the system is minimized using the hftn algorithm and then equilibrated for 1 ns while the temperature is controlled by the Nosé–Hoover thermostat at 0 Kelvin in a NVT ensemble. After equilibration, deformation at different rates associated to tension, shear, bending or torsion is applied on the boundaries as schematized in Fig. 6 for each case respectively. In our CM analysis, a beam element represents two glucose molecules (two rings); however, our mesh sensitivity analysis (Appendix A4) shows that larger element size can also be employed.

First, three simple tension tests in x , y and z directions are performed where dominant stiffness factor in the x direction is the presence of VdW forces, K_{1n} , in the y direction are VdW forces and h -bonds, K_{2n} , and in the z direction is mainly governed by the covalent bond (EA). For each test, the displacement is applied at the corresponding atoms lying on the selected boundaries. For tension in the z direction, the displacement is applied on the two cellulose rings of each chain on right side of the crystal (right boundary) while the left boundary is kept fixed as shown in Fig. 6(a). For tension in the x and y direction, the atoms lying on the top and right boundaries shown in Fig. 6(b) and (c), respectively, are displaced while their opposite surface are kept fixed. We employ different strain rates (i.e., 5.0×10^{-5} and 2.0×10^{-4} , 1.0×10^{-4} ps $^{-1}$) to ensure that quasi-static equilibrium is satisfied. Finally, the total tensile forces in x , y and z directions are obtained by summation of forces in the x , y and z directions (f_x , f_y and f_z , respectively) over corresponding boundary atoms as shown in Fig. 6. We consider that the equilibrium condition is satisfied if the difference between the absolute value of the total force on the moving and the fixed boundaries is less or equal than 0.1%.

The stress-strain curves for the tension tests in x , y and z directions are shown in Fig. 7(a)–(c), respectively. The elastic modulus for tension in the x direction, E_x , predicted by MD is 6.0–7.0 GPa while results from our model varies from 3.2 to 5.35 GPa as shown in Fig. 7(a). The relationship between E_x and our model parameters are as follow (see analytical derivation in Appendix A1).

$$E_x = (K_{1n} \sin^2 \alpha) \frac{b}{a} \quad (11)$$

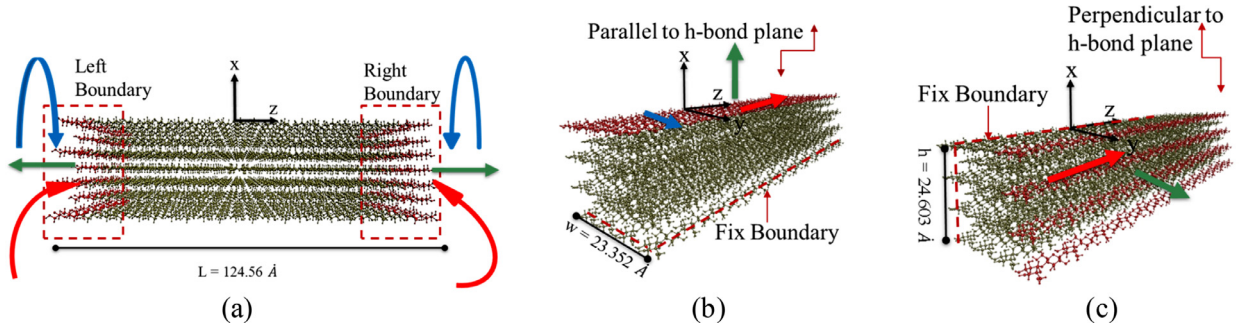


Fig. 6. Details of the MD model and boundary conditions for a 3×3 square CNC. (a) Tension, bending and torsion displacements are applied on right and left boundaries. The green, red and blue arrows show the direction of tensile, bending and torsion displacement. (b) Displacement for $shear_{xz}$ is applied parallel to h -bond plane on top surface, red arrow, while the opposite surface is kept fixed. Blue arrow shows the displacement direction for $shear_{xy}$ and the direction of tension displacement for $tension_{xx}$ is shown with green arrow. (c) Displacement for $shear_{yz}$ is applied perpendicular to h -bond plane on right surface, red arrow, while the opposite surface is kept fixed. Green arrow shows the displacement direction for tension test in y -direction. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article).

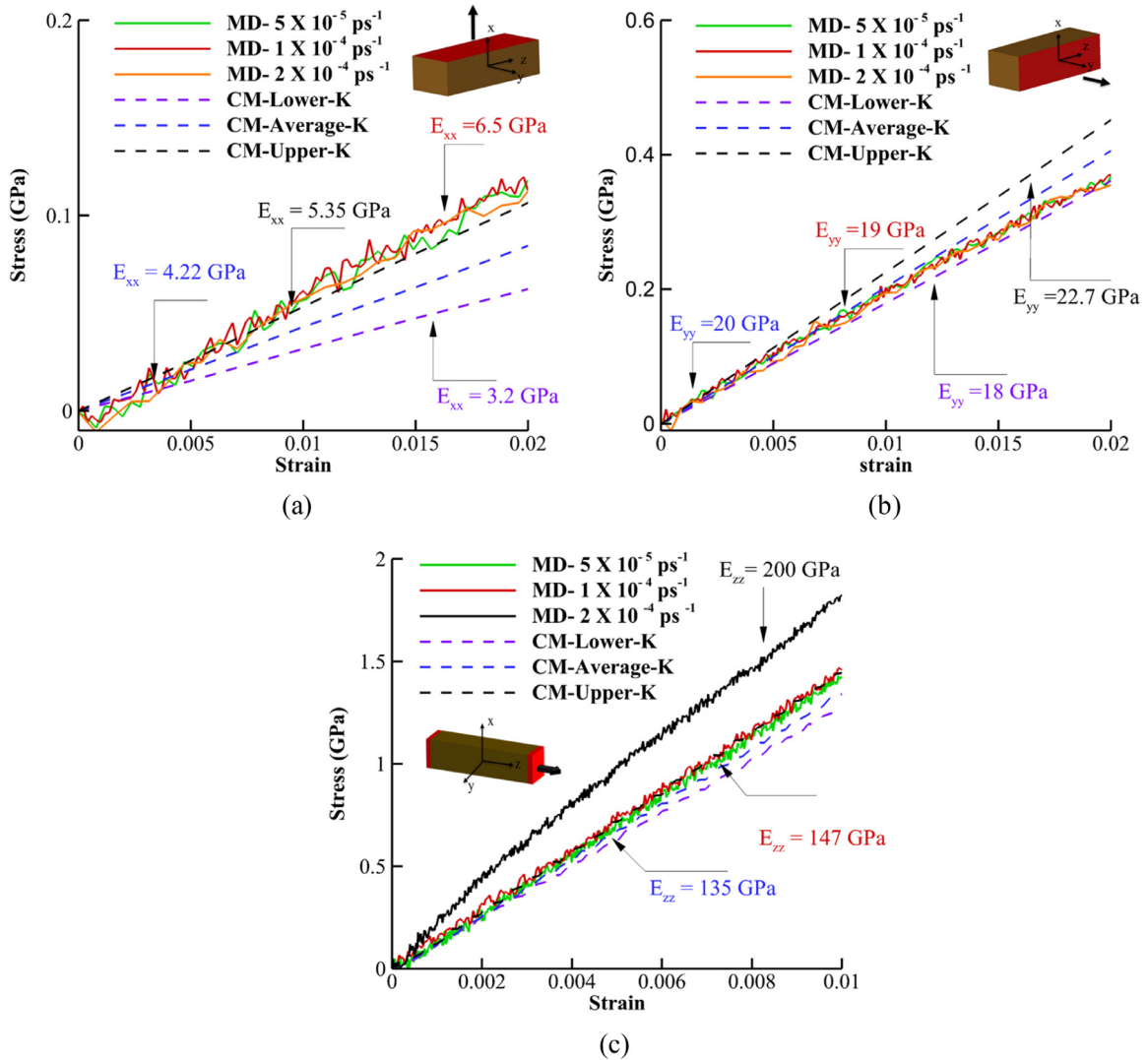


Fig. 7. Stress-strain curves for tension test. Comparing continuum model (CM) with molecular dynamics (MD) with different rates. (a) x direction (b) y direction and (c) z direction.

Where α , b , a are geometric parameters shown in Fig. A1.3(a) and K_{1n} is the inter-plane normal stiffness explained above in Section 3.2. For a perfect crystalline shape the values for a , b and α are 0.8201 nm, 0.7784 nm and 43.5° respectively which suggests a range of 2.5–4.5 GPa for E_x . This lower values of E_x with respect to the CM results may be due to the fact that after equilibrium the geometrical values, α , b , a , are different. For example the average value of E_x from Eq. (11) is 3.5 GPa while our CM model predicts 4.22 GPa due to the change in geometric parameters ($a=0.8$ nm, $b=0.85$ nm and $\alpha=50^\circ$) after equilibration. Comparison of the results with MD indicates 33% of error for average value of E_x in our CM model. One reason for underestimating the value of K_{1n} is the absence of any h -bond force in the x direction, while in MD there are few weak h -bond contributing to E_x as shown in Fig. 4. In contrast, considering the contribution of the h -bond stiffness in the x direction (which is equivalent to approximately 3 nN/nm²) to the K_{1n} , the average value from the CM model for E_x becomes 6.0 GPa which is more consistent with the MD results (6.0–7.0 GPa). Consequently, the range of E_x according to Eq. (11) becomes to 3.5–6.5 GPa.

The stress-strain curves to calculate for E_y are shown in Fig. 7(b). The values from CM vary from 18 to 22.7 GPa which is consistent with the 17–22 GPa obtained by MD. The analytical solution for E_y based on our model parameters and the simple spring and mass model presented in Appendix A1 is

$$E_y = \left[(K_{1n} \cos^2 \alpha) + \left(\frac{m+1}{m} + \frac{n-1}{n} \right) K_{2n} \right] \frac{a}{b} \quad (12)$$

where α , b , a are the geometric parameters shown in Fig. A1.3b. K_{1n} and K_{2n} are the inter-plane and in-plane normal stiffness discussed in Section 3.2. The parameters m and n are the number of repeated unit cell in the CNC structure (e.g. here m and n are both equal to 3). For a perfect CNC structure, Eq. (12) predicts $E_y = 26$ –36 GPa, which indicates that the potential imperfection introduced by equilibration could reduce elastic modulus in the y direction by 30%. In addition, from Eq. (12) and knowing the value for h -bond stiffness, we infer that the contribution of h -bond in E_y is around 50% and the other half is provided by VdW forces.

For the stiffness in the z direction, Fig. 7(c), we observed strain rate dependent elasticity for 2.0×10^{-4} ps⁻¹ strain rate and higher where equilibrium is no longer satisfied. Due to the fact that bonded and non-bonded interactions are separated in the continuum model, their contribution in the total stiffness can readily be studied by turning on/off non-bonded elements. Interestingly, the same stress-strain response is obtained when we turn off the non-bonded elements, indicating that the stiffness is mainly driven by the covalent bond and intra-chain h -bonds. There is a negligible difference between continuum and MD curves (~8% in the elastic modulus). A simple analytical model for CNC with a h -bonding network A (Nishiyama et al., 2002), is presented in Appendix A1 to evaluate the effect of inter-chain h -bond on the total stiffness of CNCs. The results indicate that the contribution of the inter-chain h -bond in the axial stiffness for a 3×3 CNC is approximately 3%, and less than 5% contribution for a large $m \times n$ crystal. Therefore, we conclude the remaining 5% of difference in elasticity is coming from the estimation of chain stiffness. The analytical expression for E_z based on the simple model presented in Appendix A1 is given by

$$E_z = \frac{[(m+1)(n+1) + mn]EA}{(ma \times nb)} \quad (13)$$

Considering $m=n=3$ then E_z as 126–142 GPa which has a good agreement with the CM, 123–147 GPa, and MD, 141–153 GPa, results presented in Fig. 7(c). In addition, from Eq. (13), and assuming that chain stiffness, EA , is constant for different values of m and n ; the variation of elastic modulus, E_z , with respect to the size of CNC can be plotted as shown in Fig. A1.2b. The values of E_z varies from 250 GPa to 100 GPa for $m=1$ and a large value of m respectively. The typical size associated with a typical CNC size is indicated in Fig. A1.2b with green rectangle suggesting a range of 115–135 GPa for E_z .

To further study the mechanical behavior of the CNC, we load it in shear along three different directions and at different strain rates (i.e., 2.0×10^{-4} , 5×10^{-4} and 2.0×10^{-3} ps⁻¹). For a simple shear test, the displacement is applied on one surface while the opposite surface is kept fixed while equilibrium condition is satisfied. The total shear stress is then obtained as the summation of all the corresponding individual forces on the surface of interest divided by its area. In the $shear_{xy}$ test, the displacement is applied on top surface in the y direction and parallel to h -bond plane as shown with blue arrow in Fig. 6(b). The stress-strain curves of CM and MD simulations for $shear_{xy}$ are shown in Fig. 8(a). The value for the shear modulus from MD simulation is $G_{xy} = 1.9$ –2.9 GPa, while the CM provides a range of $G_{xy} = 1.2$ –2.2 GPa. To understand what parameters in our CM model affects the G_{xy} , a simple analytical solution from a spring-mass model for $shear_{xy}$ is employed (Appendix A2) as follow

$$G_{xy} = (K_{1n} \cos^2 \alpha) \frac{b}{a} \quad (14)$$

Similar to the case with tension in the x direction, K_{1n} is responsible for the elastic modulus and should be corrected by adding h -bond stiffness in the x direction. After adding h -bond stiffness, for CM new range of values is 1.8–3.2 GPa, which is consistent with MD results. From Eq. (14) the theoretical value of G_{xy} for a perfect CNC structure is 3.75–5.75 GPa with a , b and α equal to 0.8201 nm, 0.7784 nm and 43.5° respectively. Further analysis shows that 30% of G_{xy} is provided by the h -bond stiffness and 70% by the VdW interaction. For G_{xz} test, displacement is applied on top surface and in the z direction, parallel to h -bond plane as shown with red arrow in Fig. 6(b). The stress-strain curves for G_{xz} obtained from the MD and CM simulations are shown in Fig. 8(b), which indicate that the corresponding shear modulus, G_{xz} , is 2.0–2.6 GPa from the

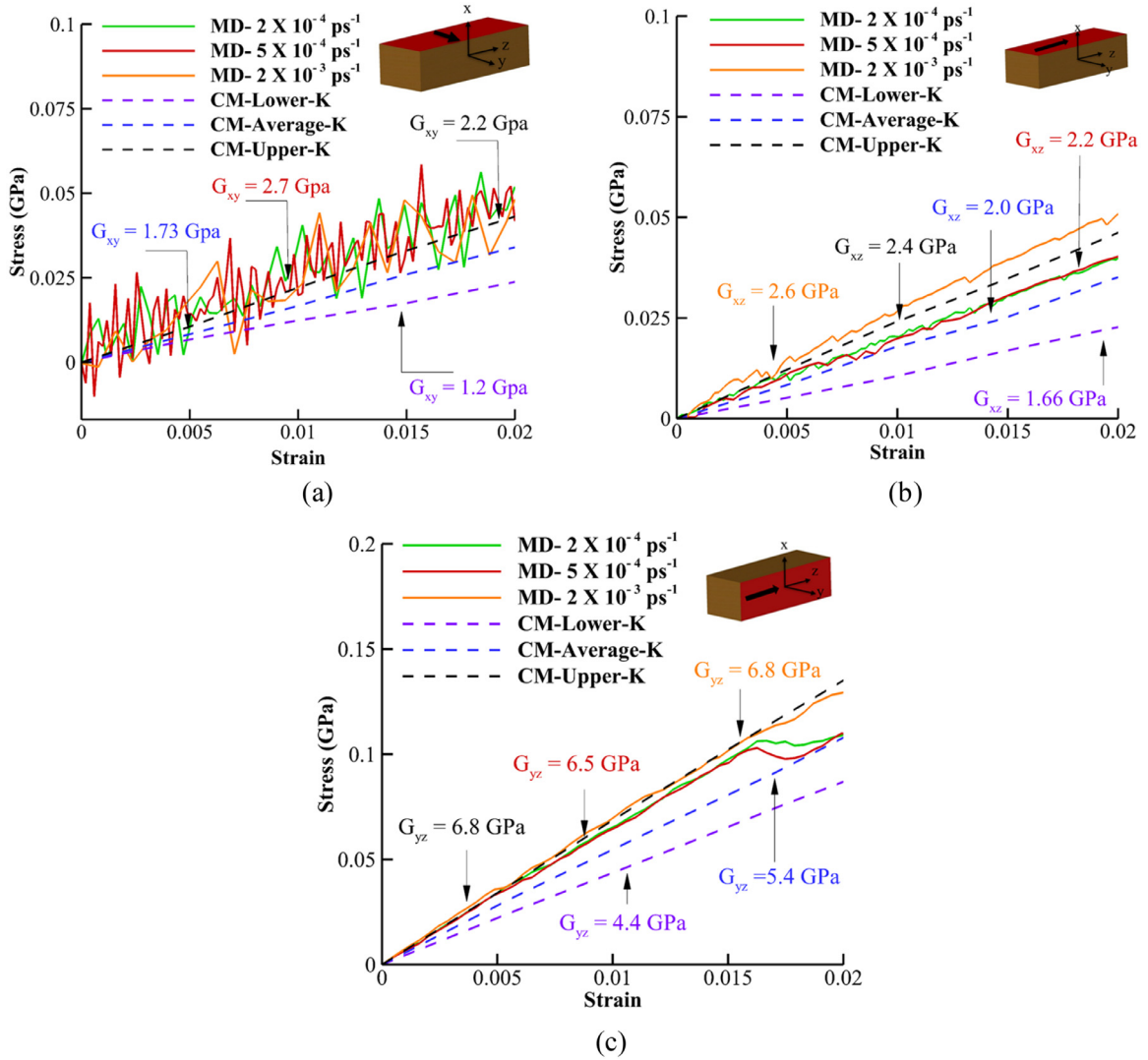


Fig. 8. Stress-strain curves for shear tests from MD with different rates and CM with upper and lower bound obtained from upper and lower bound of stiffness respectively. (a) Stress-strain curves for $shear_{xy}$ (b) $shear_{xz}$ and (c) $shear_{yz}$.

MD simulation, while the CM simulations exhibit a range of 1.6–2.4 GPa. A simple spring-mass model helps elucidate the shear mechanisms in CNC (Appendix A2). Accordingly,

$$G_{xz} = \frac{K_{1t}b}{a} \quad (15)$$

This analytical expression yields G_{xz} 1.3–1.9 GPa, which is close to CM and MD results. This indicates that G_{xz} is not too much affected by the geometrical change due to the equilibration. The third shear test is G_{yz} , where the displacement is applied on the right surface in the z direction, perpendicular to h -bond planes, as shown with red arrow in Fig. 6(c). The stress-strain curves for G_{yz} are plotted in Fig. 8(c) for MD and CM. The value for shear modulus, G_{yz} , from MD is 6.5–6.8 GPa, while CM predicts a range of G_{yz} = 4.4–6.8 GPa. The analytical model for G_{yz} gives us the relationship between G_{yz} and our model parameters as follow (Appendix A2):

$$G_{yz} = \left[K_{1t} + \left(\frac{m+1}{m} + \frac{n-1}{n} \right) K_{2t} \right] \frac{a}{b} \quad (16)$$

Where b , a are geometric parameters shown in Fig. A2.1. K_{1t} and K_{2t} are the inter-plane and in-plane shear stiffness explained in Section 3.2. From Eq. (16) the shear modulus, G_{yz} , for the perfect CNC structure is predicted as 5.6–8.4 GPa, which indicates that the change in the CNC structure during equilibration has little effect on the G_{yz} .

Two bending tests are also performed to understand the mechanical performance of CNC under bending in the x and y direction. For both tests, the moment is applied at the end of the CNC by applying rotational displacements at different

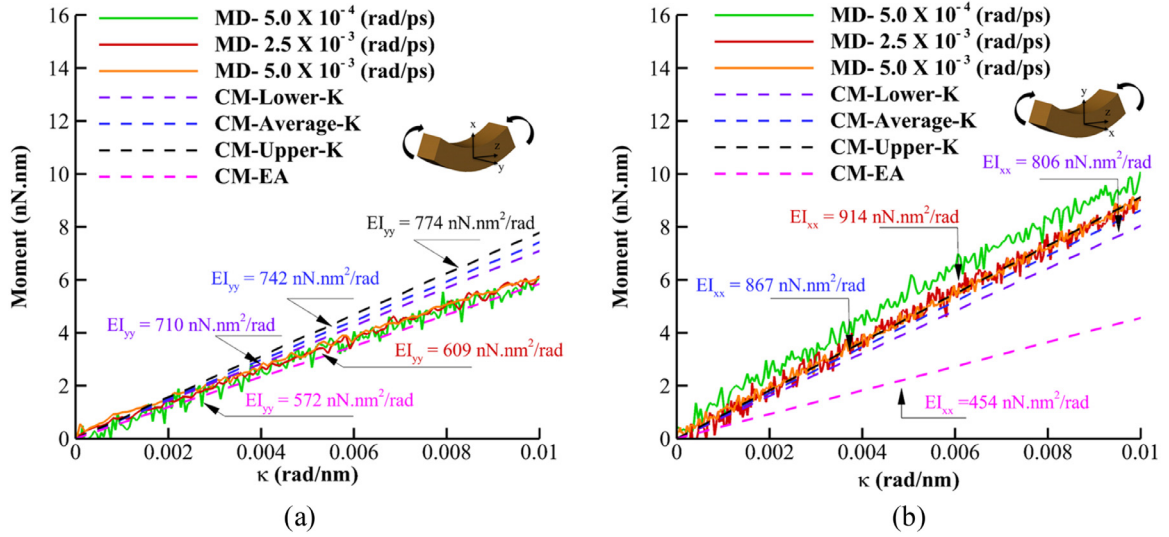


Fig. 9. Moment-curvature plots for bending of CNC obtained from MD and CM simulations with different rates and different stiffness respectively. (a) pure bending around y-axis, which is parallel to the *h*-bond plane. (b) Pure bending around x axis which is perpendicular to the *h*-bond plane.

rates (i.e., 5.0×10^{-4} , 2.5×10^{-3} and 5.0×10^{-3} rad/ps) on the first two rings of each chain on the right and left hand side of the crystal (see red arrows in Fig 6(a)). In such a way, the boundary atoms move similar to boundaries in a pure bending test. For pure bending around the y direction, parallel to the *h*-bond plane, the bending moment is calculated as

$$M_y = \sum_1^{nbc} (z \times f_x - x \times f_z) \quad (17)$$

Where M_y is the bending moment in y direction, nbc is the number of atoms at boundary, z and x are the distance of each boundary atoms from the z and x axes, respectively (the origin of the system of coordinates is located at the centroid of the CNC). Finally f_x and f_z are total forces on each boundary atoms in x and z direction, respectively. To understand the effect of covalent bond on the bending stiffness, we analyze the CM model with and without non-bonded stiffness. Moment-curvature plots for pure bending around y-axis obtained from MD and CM simulations are shown Fig. 9(a). The bending stiffness around the y axis calculated with MD is $EI_{yy} = 550\text{--}800$ nN.nm²/rad and from CM is $EI_{yy} = 742$ nN.nm²/rad on average with upper bound and lower bound of 710 and 774 nN.nm²/rad respectively. The parameters involved in our model for EI_{yy} are EA (chain stiffness) and K_{1t} (inter-plane shear stiffness, which is also the main parameter for G_{xz}). As expected, during bending deformation around the y axis, the chains on top and bottom of y axis experience compression and tension, respectively. As such, the high axial stiffness of the individual cellulose chains significantly contributes to overall bending stiffness. From this perspective, a simple spring-mass model can be developed based on the single cellulose chain stiffness, EA, (see Appendix A3):

$$M = \frac{26h^2EA}{9} \left(\frac{\theta}{L} \right) \quad (18)$$

Where θ is the bending angle, EA is stiffness of each chain, h is the height of the cross section and L is the length of each chain. By replacing the values for EA and h in Eq. (18), the bending stiffness, $EI_{yy} = 487$ nN.nm²/rad. This value is lower than the value 572 nN.nm²/rad, pink dash line in Fig. 9(a), obtained from CM with no non-bonded stiffness. We surmise that this difference is coming from considering a perfect CNC structure (i.e., with exact dimensions as previously reported in the literature), while the CM model employs the position of the chain based on the ones predicted by MD after equilibration. For instance, the value of $h = 2.55$ nm in the CM model is 7% larger than the actual value used in the analytical equation $h = 2.335$ nm. If we use $h = 2.55$ nm in the analytical equation, then a value of $EI_{yy} = 582$ nN.nm²/rad, which is similar to those obtained with CM. Comparing the results for CM with average value of non-bonded stiffness and the case with no non-bonded stiffness, we conclude that 23% of the value for average EI_{yy} in the CM model is due to non-bonded stiffness, K_{1t} , and 77% from the EA (intra-chain *h*-bond and covalent bond). In addition, comparing the results from MD with CM-EA (only chains stiffness (EA) contribute with no non-bonded contribution) shows that non-bonded interactions represent less than 20% of the overall value of EI_{yy} . Eq. (18) can be further reduced considering the second moment of inertia of solids, $I = \frac{1}{12} wh^3$, and curvature $\kappa = \frac{\theta}{L}$ to

$$M \cong f \cdot E_z I \kappa \quad (19)$$

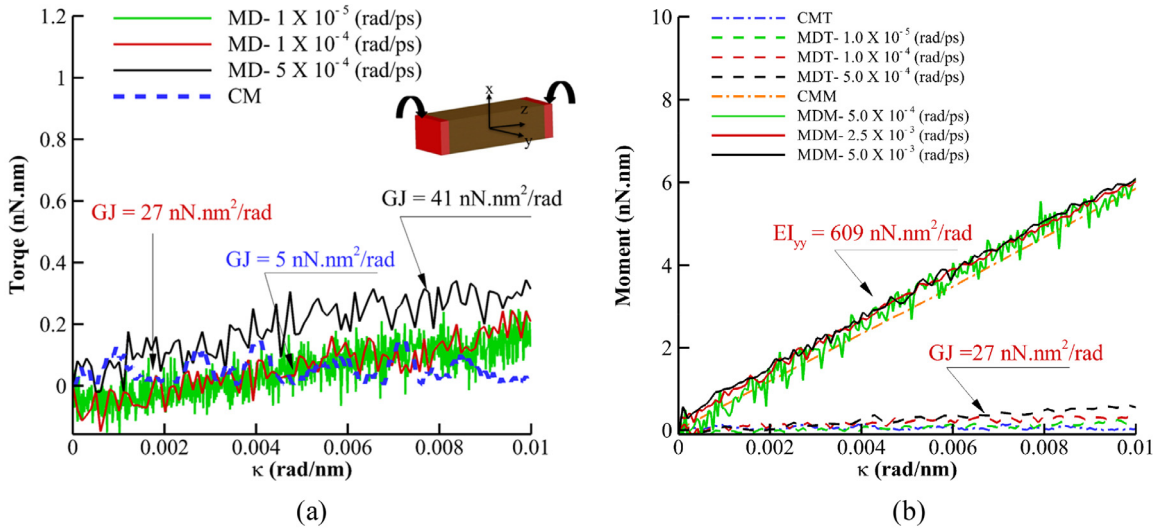


Fig. 10. (a) Torque-twist angle per length curves for torsion test with different torsion frequencies for MD and continuum. (b) Same results in bending scale.

where for this particular case $f=4/3$. This general expression is similar to that obtained for isotropic solids (e.g., $M=El\kappa$) expect that $f=1$. The values for f for a square shape ($n=m$) with different values of m are plotted in Fig. A3.2. The f value merges to 1, similar to solids, as the dimension increases and has the highest value of 2.4 for $m=n=1$. The value of f for typical CNC size is 1.2–1.4 with average of 1.28 for $m=4$ with 41 chains.

Similarly, we analyze bending around the x axis, perpendicular to the h -bond plane. In this case, the bending moment is calculated as

$$M_x = \sum_1^{nbc} (z \times f_y - y \times f_z) \quad (20)$$

Where M_x is the bending moment in x direction, nbc is the number of atoms at boundary, z and y are the distance of each boundary atoms from z and y axes, respectively (the origin is the centroid of the CNC). Fig. 9(b) exhibits the moment-curvature plots for pure bending around the x axis. MD predicts $El_{xx} = 800$ – 1000 nN.nm²/rad, while CM values are $El_{xx} = 806$ – 916 nN.nm²/rad. Eq. (18) can also be used to estimate El_{xx} , by changing h to w , when there are no non-bonded interactions involved. In such case, the estimated value for from Eq. (18) is $El_{xx} = 435$ nN.nm²/rad, which agrees very well with the value reported by CM with non-bonded stiffness (i.e., $El_{xx} = 454$ nN.nm²/rad). The parameters involved in our model for El_{xx} are EA and K_{2t} (in-plane shear stiffness which is also the main parameter for G_{yz}). By comparing the results obtained with CM with average stiffness and CM with no stiffness, it can be concluded that 52% contribution to El_{xx} is provided by EA (coming from intra-chain h -bond and covalent bond) and the rest is from K_{2t} (non-bonded interactions). Also by comparing the CM results with MD, we can conclude that, in the case of El_{xx} , bonded and non-bonded interactions have equal contribution to bending stiffness as opposed to the El_{yy} case, where EA is almost the only contribution to the overall bending stiffness.

A final test is to subject a CNC to a torsion loading. In this case the angular displacements are directly applied to the left and right boundaries, as shown with blue arrows in Fig. 6(a), at different rates including (i.e., 1.0×10^{-5} , 1×10^{-4} and 5.0×10^{-4} rad/ps). The torque is then obtained as follows:

$$T = \sum_1^{nbc} (xf_y - yf_x) \quad (21)$$

Where T is the torque, nbc is the number of atoms at the boundary, x and y are the distance of each boundary atoms from x and y axis, respectively, with respect to the origin, which is located at the center of mass. f_x and f_y are total forces on each boundary atoms in x and y directions, respectively. The total torque, T , versus twist deformation per unit length, κ , for MD and CM are shown in Fig. 10(a). The estimated value for GJ from MD is 10–50 nN.nm²/rad, while CM suggests negligible torsional stiffness (0–10 nN.nm²/rad). We realized that the only parameter in our CM that has influence on GJ is El_c (bending stiffness of the chain). However, the value of the torque obtained with the CM model always fluctuate. The main reason for this fluctuation may be the small value of GJ in CNC. In fact, Fig. 10(b) clearly shows that the bending stiffness, El_{yy} , is larger than the torsional stiffness, GJ . The fact that GJ is one order of magnitude smaller than El_{yy} suggests that CNCs could twist easily even under small loads which could also explain the tendency of CNCs to naturally twist without external loads (Hanley et al., 1997; Lotz and Cheng, 2005; Hadden et al., 2013; Zhao et al., 2013).

Table 1
Elastic properties of CNC based on spring-mass model.

Elastic property	Formulation	Values for a perfect CNC (GPa)	Values from MD (GPa)
E_x	$(K_{1n} \sin^2 \alpha) \frac{b}{a}$	5 ± 1.5	6.5
E_y	$[(K_{1n} \cos^2 \alpha) + (\frac{m+1}{m} + \frac{n-1}{n}) K_{2n}] \frac{a}{b}$	31 ± 5	19
E_z	$\frac{[(m+1)(n+1)+mn]EA}{(ma \times nb)}$	134 ± 8	147
G_{xy}	$(K_{1n} \cos^2 \alpha) \frac{b}{a}$	4.75 ± 1	2.7
G_{xz}	$K_{1t} \frac{b}{a}$	1.6 ± 0.3	2.0
G_{yz}	$[K_{1t} + (\frac{m+1}{m} + \frac{n-1}{n}) K_{2t}] \frac{a}{b}$	7 ± 1.4	6.5

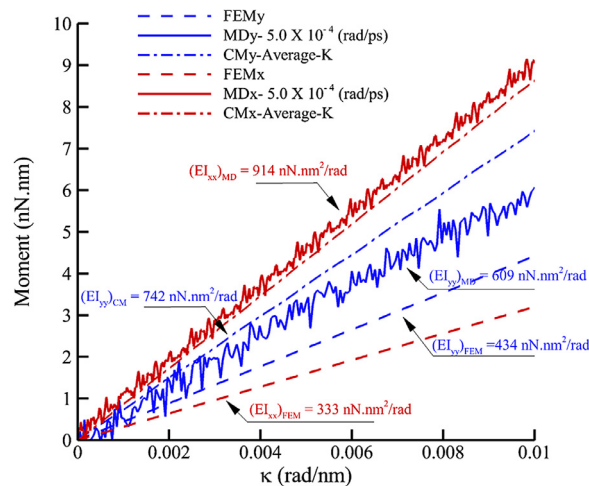


Fig. 11. Moment-curvature plots for bending of CNC around x and y axis acquired from CM, MD and FEM simulations. The solid curves show MD results, dashed lines are FEM results and dashed-dot lines present CM results. The lines with blue and red color represent bending around y and x axis respectively. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

Table 1 summarizes the analytical expressions presented in the Appendix section for the elastic properties of CNC based on the spring constants, EA , K_{1t} , K_{1n} , K_{2t} , K_{2n} and geometric properties. The table also includes the value obtained for the perfect crystal, and the comparison with the MD results. While the differences with respect to the MD results are mainly due to structural change after MD equilibration, these results are very encouraging. This demonstrate that fundamental elements of conventional solid mechanics can be employed to explain the contributions of the different bond types on the overall stiffness of CNCs. In order to illustrate whether the details of the chains and non-bonded interaction are needed, we model a CNC under bending employing FEM and treating the CNC as a homogeneous and orthotropic solid. To increase accuracy, we use the elastic properties obtained from MD simulations (taken from the fourth column in Table 1). This homogenized model (denoted as FEM) is different from the CM model in the sense that it assumes the CNC is only a homogeneous orthotropic solid with no structure inside. Fig. 11 compares the values E_{xx} and E_{yy} obtained from MD, CM with average stiffness and FEM. By comparing the FEM and MD, as it can be observed, the FEM model clearly underestimates the bending stiffness in both directions. Although the value for E_{yy} predicted by FEM, $434 \text{ nN.nm}^2/\text{rad}$, is comparable with MD, $609 \text{ nN.nm}^2/\text{rad}$, the results for E_{xx} , $333 \text{ nN.nm}^2/\text{rad}$, is very different from value obtained from MD simulation ($914 \text{ nN.nm}^2/\text{rad}$). In fact, the value of E_{xx} obtained with the FEM results agrees with the CM model for the case without non-bonded stiffness (i.e., $K_{2t} = 0$), $E_{xx} = 454 \text{ nN.nm}^2/\text{rad}$, as seen as a pink dash line in Fig. 9(b). In summary, although FEM can model the contribution of EA (chain stiffness) to the E_{xx} and E_{yy} through E_z in an orthotropic material, it fails to properly capture the contribution of non-bonded interaction.

5. Summary and Conclusions

In this paper, a continuum-based structural model was developed to investigate the role of bonded and non-bonded interactions on mechanical properties of crystalline cellulose for small strains. In particular, bonded and non-bonded interactions were uncoupled in our continuum model and substituted by an equivalent continuum element. Ancillary atomistic simulations were employed for feeding the continuum model parameters and also for verification purposes. We performed a variety of mechanical tests including tension, shear, bending and torsion to understand the deformation mechanism and contribution of each type of bonding on the elastic behavior of CNCs. For most of the cases, analytical expression for perfect

CNC structure were proposed to understand how imperfection in the structure after equilibrium, due to finite size of CNC, would affect the elastic properties. In addition, the deformation mechanism of CNC can be better understood and verified by deriving analytical expressions of the most important elastic properties. The initial assumption that bonded and non-bonded interactions could be decoupled was later validated by our simulations and analytical equations (see Table 1 and Appendix A1–A3). Our results indicated that individual axial stiffness of the chains (i.e. EA) was the main contributor to the overall mechanical properties of CNC. For instance, we showed that the overall EA of a CNC is practically given by the sum of the EA from the individual chains (Appendix A1). This was demonstrated by showing (1) that the inter-chain h -bonding has a minor effect on the total stiffness of CNC (less than 5%) and (2) that our analytical expression for E_z for a CNC, which is only based on the individual chains' EAs, is consistent with the CM and MD results.

Three tension tests along the x (i.e., VdW dominant), y (h -bond dominant), and z (i.e., covalent bond dominant) directions were performed. We first consider the contribution of VdW forces in the x direction, which leads to 35% error in comparison with MD in the prediction of E_x . However, after adding the h -bond stiffness, such error was reduced to only 5%. We showed that the analytical solution for E_x is indeed in the range of the values obtained with MD, showing that imperfections due to equilibration process has little effect on the values. For elastic modulus in the y direction, both CM and MD predict 18–22 GPa, which is below the predicted value by analytical solution for perfect crystal ($E_y = 26$ –36 GPa). This shows that the imperfection due to equilibration could reduce the elastic modulus in the y direction by 30%. In addition we conclude that the contribution of h -bonds to E_y is approximately 50% and the other half is provided by VdW forces. For tension in the z direction, the results indicate that only covalent bond and intra-chain h -bonds are the main source of stiffness in E_z . On the other hand, inter-chain h -bond or VdW forces contribute to less than 5% to the overall stiffness. The analytical solutions for E_z were shown to agree reasonably well with the MD results, indicating that the imperfections introduced to equilibration in the MD process have a negligible effect on E_z . In addition, the analytical solutions suggests that E_z is size dependent with values of 100–250 GPa for very narrow and wide CNCs respectively and a range of 115–135 GPa for typical CNC size.

The analysis of shear deformation showed a similar agreement between CM and MD. For $shear_{xy}$, the results indicate that 30% of G_{xy} is provided by h -bond stiffness and 70% by VdW interaction. However, the analytical solution for G_{xy} in a perfect crystal is 40% higher than MD results, demonstrating that G_{xy} is sensitive to deviations of the structure from the perfect crystal. For both $shear_{xz}$ and $shear_{yz}$, only VdW interactions contribute to the shear modulus (G_{xz} and G_{yz}). In $shear_{xz}$ only inter-plane VdW stiffness (i.e., Eq. (15)) affects the value for G_{xz} . However, for $shear_{yz}$ both, in-plane and inter-plane shear stiffness (i.e., Eq. (16)), contribute to G_{yz} . This effect leads to higher G_{yz} , 6.5 GPa, in comparison with the G_{xz} (2.0 GPa). Also the comparison of the shear modulus calculated from the analytical solutions (Eqs. (15) and (16)) with the MD results, suggests that structural imperfections due to equilibration have little effect on G_{xz} and G_{yz} . Analysis of the bending test around the y axis indicates that the non-bonded interactions are very unlikely to contribute to El_{yy} (e.g., less than 20%). However, the same indicates that more than 80% is mainly provided by EA. By comparing the CM results with MD, for both bending tests, we can conclude that in the case of El_{xx} , bonded and non-bonded interactions have equal contribution to bending stiffness. This is in contrast with the case of El_{yy} , where EA is almost the only contributor. As a result, the value for El_{xx} is 1.5 times more than El_{yy} . Comparing the CNC with equivalent solid size in bending, $f = M/\kappa E_z I$, indicates that as the cross section of CNCs increase, they behave similar to solids in bending, $f = 1$, but for a typical CNC size the bending behavior is superior to solids ($f = 1.2$ –1.4). The results show very small torsional stiffness in CNC, which indicates its tendency to twist even under very small torques (Hanley et al., 1997; Lotz and Cheng, 2005; Hadden et al., 2013; Zhao et al., 2013). Finally we investigated an orthotropic model using FEM for comparison purposes. Our results show that, although FEM can capture the contribution of EA (chain stiffness) to the El_{xx} and El_{yy} , it fails to capture the contribution of the non-bonded interaction. This case is more noticeable in El_{xx} .

In summary, this work introduces a simplified continuum-based structural model (CM) that can be implemented under the finite element framework to capture the elastic response of CNC. This first elastic model, together with the analytical models, was shown to be very useful in predicting the different elastic properties and elucidating the main mechanisms that contribute to the overall stiffness of the CNC under various loading conditions. This is a first step toward the development of a model that could also capture the non-linear and inelastic behavior of CNC by considering debonding of the non-bonded elements. Future work will focus on developing cohesive zone type of models for the debonding between chains and even breakage of the covalent bonds. In addition, as a future work, the effect of temperature and environment (e.g., influence of water) on the mechanical properties of CNC can also be incorporated to the proposed model. For example, almost all the studies on CNC in a water solvent confirmed that the interaction of CNC and water is mostly limited to the surface of the CNC and that water molecules could not get inside the CNC (Matthews et al., 2006; Lahiji et al., 2010).

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Appendix

A1. Tensile stiffness

We present a simple analytical model to understand the effect of inter-chain *h*-bond and to support the comparison between the CM and MD models. Fig. A1.1(a) and (b) represent simple spring model for inter-chain *h*-bond for the center and origin chains respectively (See Fig. 1). Covalent and intra-chain *h*-bonds in each chain are modeled together as one elastic bar, green lines in Fig. A1.1, and inter-chain *h*-bonds are replaced with springs, which are shown in Fig. A1.1 as blue springs. Based on the orientation of inter-chain *h*-bonds in center planes, both chains and *h*-bonds contribute to the axial stiffness. However, only the chains contribute to the total stiffness in the origin planes due to the fact that the *h*-bonds are perpendicular to longitudinal axis. While value for stiffness for the chains can be obtained directly from the MD results presented in Section 3.2, the stiffness of each spring can be assumed to be αk , where α is a dimensionless coefficient and k the stiffness of each chain. As such, the total stiffness, K_{t1} , and *h*-bonds stiffness, K_{h1} , of the one dimensional (1D) representation of the center plane shown in Fig. A1.1(a) are obtained as follows:

$$\frac{1}{k_{t1}} = \frac{1}{3 \times 5k} + \frac{1}{2\alpha k + 3 \times 5k} + \frac{1}{3 \times 5k} + \frac{1}{2\alpha k + 3 \times 5k} + \frac{1}{3 \times 5k} \quad (A1.1)$$

$$K_{t1} = \frac{75k + 10\alpha k}{25 + 2\alpha} \quad (A1.2)$$

$$K_{h1} = 0.5 \times \left(\frac{75k + 10\alpha k}{25 + 2\alpha} - 3k \right) = \frac{2\alpha k}{25 + 2\alpha} \quad (A1.2)$$

The total stiffness of the $m \times n$ crystalline cellulose can be obtained by taking into account the total number of chains, $(m+1)(n+1) + mn$, and 1D representations, $m(n-1)$, in the crystal.

$$K_t = K_h + K_c = m(n-1)K_{h1} + [(m+1)(n+1) + mn]k \quad (A1.3)$$

Where K_h and K_c are the total contribution of inter-chain *h*-bond and chains in total stiffness respectively. To better show the inter-chain *h*-bond contribution, ΔS , is defined as the normalized inter-chain tensile stiffness over total tensile stiffness.

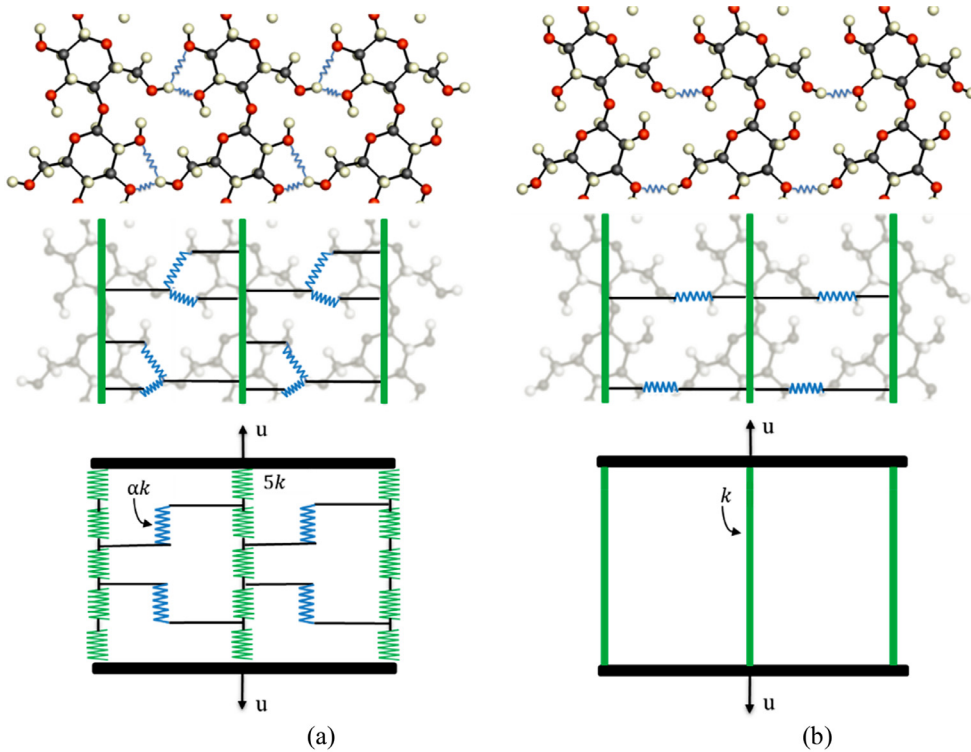


Fig A1.1. Schematic representation of the conversion from an atomistic model to a 1D spring model for (a) center plane and (b) origin plane (See Fig. 1). In the top figure inter-chain *h*-bonds replaced by linear springs. In middle figure cellulose chains replaced by bar members. In bottom Fig. 1 D model in axial direction is obtained.

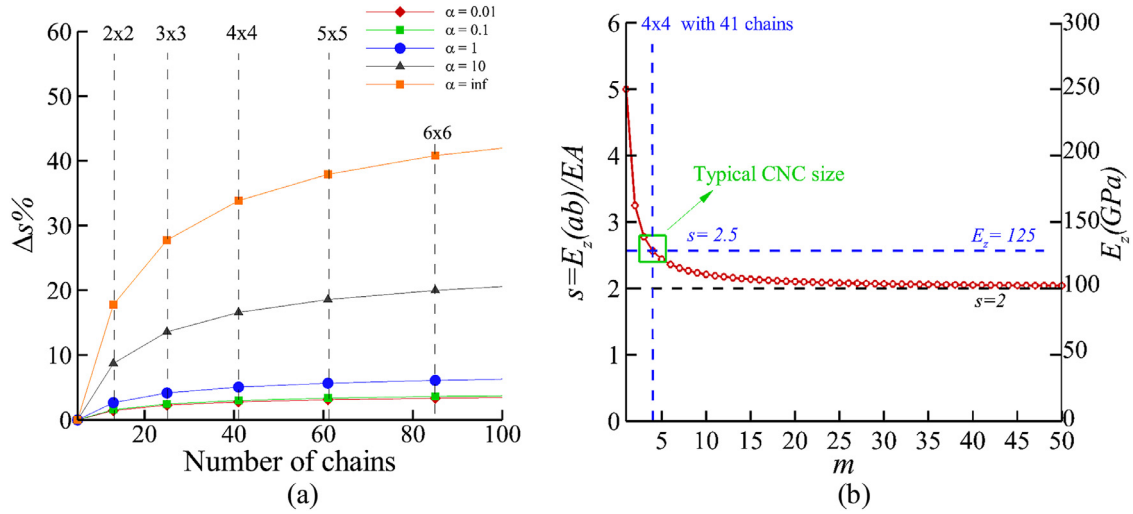


Fig A1.2. (a) Normalized stiffness (ΔS) as function of α and number of chains (b) Variation of s parameter and elastic modulus with respect to size of CNC (m).

$$\Delta S = \left(\frac{K_t}{K_c} - 1 \right) \times 100 = \left(\frac{K_h}{K_c} \right) \times 100 \quad (\text{A1.4})$$

The variation of ΔS as a function of number of chains in a crystal and for different values of α is shown in Eq. (A1.2). Based on our MD simulation, Fig. 5., the value of α is approximately 0.1, which translates into a total contribution of inter-chain h -bond to the total stiffness of less than 5% for any number of chains. Neglecting the term of the h -bonds, and assuming that only the individual chain stiffness, K_c , contributes to the total stiffness, the elastic modulus of CNC in the chain direction can be directly estimated by dividing the total force carried by the chains by the CNC cross section area as follows:

$$E_z = \frac{\sigma_z}{\varepsilon_z} = \frac{F_z}{A_t \varepsilon_z} = \frac{[(m+1)(n+1) + mn]EA}{(ma \times nb)} \quad (\text{A1.5})$$

Where A_t is the cross section Area, F_z is the total force in the chain direction, which is obtained by the product of total stiffness, K_c , and displacement. The expression in Eq. (A1.5) is obtained by replacing k in Eq. (A1.2), by EA/L , and cross section area by $(ma \times nb)$. Assuming that the stiffness of an individual chain, EA , only depends on its length and not on the size of crystal (e.g., m and n parameters), E_z can be rewritten as:

$$E_z = s \cdot \frac{EA}{ab} \quad (\text{A1.6})$$

Where $s = [(m+1)(n+1) + mn]/mn$ is a size dependent parameter. For instance, for a 3×3 case, with $a = 0.8201$ nm, $b = 0.7784$ nm and $EA = 31 \pm 2$ nN, we obtain $E_z = 134 \pm 8$ GPa, which is consistent with our MD and CM results presented in Fig. 8(a). In addition, the size dependence of E_z can be analyzed by plotting s as a function of m , as seen in Fig. A1.2(b). The size parameter, s , varies from 5 for a value of $m=1$ and $E_z = 250$ GPa, to an asymptotic value of 2 for large CNC size and $E_z = 100$ GPa. The typical size associated with a typical CNC size is indicated in Fig. A1.2(b) with green rectangle suggesting a range of E_z between 115 and 135 GPa. This range of values agrees with what has been reported in the literature previously.

The elastic modulus in the VdW (x -direction) and h -bond (y -direction) directions can also be obtained using a simple spring and mass model as the one shown in the Fig A1.3. The chains in Fig A1.3 are shown with blue circles, the red springs represent inter-chain stiffness and the green springs represent the in-plane stiffness in the h -bond direction, which is the sum of h -bond and VdW stiffness. Here we use the principle of virtual work by balancing the internal and external energy to obtain the elasticity moduli in each direction. The internal energy in the x direction, U , can be written as

$$U = 0.5 \times (K_{1n} L \sin^2 \alpha) \left(\frac{\delta}{2n} \right)^2 \times n \times m \times 4 = 0.5 F \delta \quad (\text{A1.6})$$

$$\sigma_x = \frac{F}{WL}, \quad \varepsilon_x = \frac{\delta}{h}, \quad E_x = \frac{\sigma_x}{\varepsilon_x} \quad (\text{A1.6})$$

Where F is the external force, δ is the external displacement and $\left(\frac{\delta}{2n} \right)$ is the deformation of each red spring in the x direction. By replacing F from Eq. (A1.5), $w = m \times a$, $h = n \times b$ into Eq. (A1.6) the elastic modulus can be expressed as

$$E_x = (K_{1n} \sin^2 \alpha) \frac{b}{a} \quad (\text{A1.7})$$

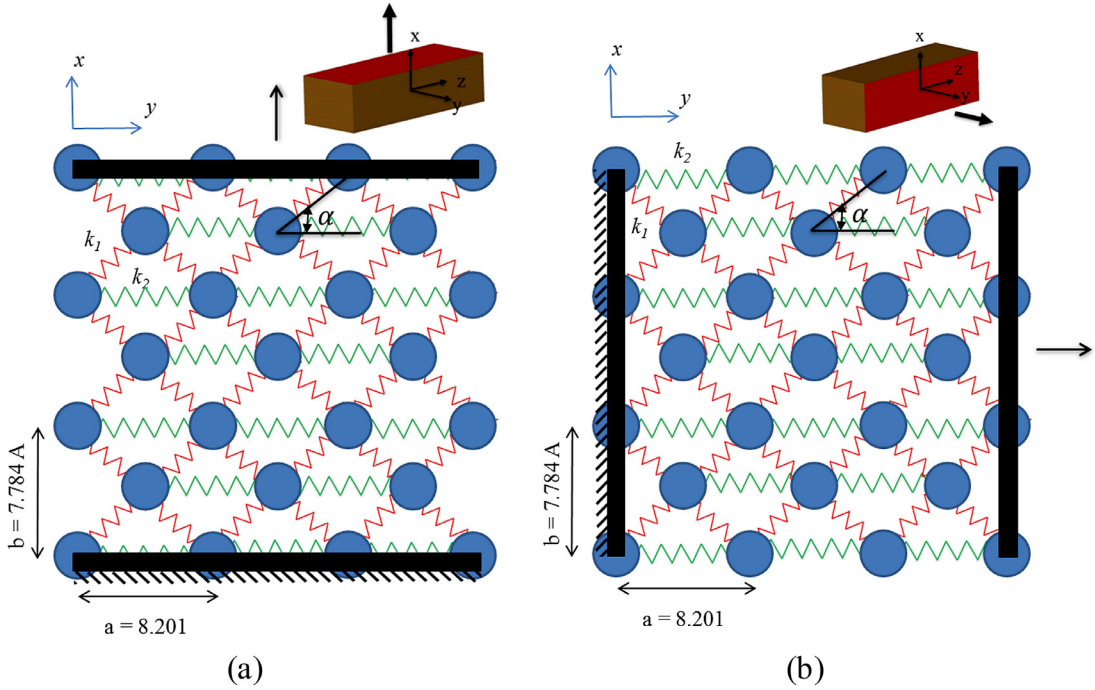


Fig. A1.3. 2D representation of the 3×3 CNC for tensile loading. Chains are shown with blue circles, stiffness in h-bond direction with green spring and stiffness in VdW direction with red spring. The boundaries for applying and fixing displacement are shown in black rectangle. (a) Applying tensile displacement on top chains in the x direction, VdW direction, while the bottom chains are fixed. (b) Applying tensile displacement on right chains in the y direction, h-bond direction, while the left chains are fixed. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article).

By using the same approach for tensile test in the y direction, the elastic modulus in the y direction can be obtained as follows

$$U = 0.5 \times (K_{1n} L \cos^2 \alpha) \left(\frac{\delta}{2m} \right)^2 \times n \times m \times 4 + 0.5 \times (K_{2n} L) \left(\frac{\delta}{n} \right)^2 \times [n \times (m+1) + (n-1) \times m] = 0.5 F \delta \quad (\text{A1.8})$$

$$\sigma_y = \frac{F}{hL}, \quad \varepsilon_y = \frac{\delta}{W}, \quad E_y = \frac{\sigma_y}{\varepsilon_y} \quad (\text{A1.9})$$

In addition to the red springs, k_1 , green springs, k_2 , also contribute to the internal energy, which is shown as the second term in Eq. (A1.8). By replacing F from Eq. (A1.8), $w = m \times a$, $h = n \times b$ into Eq. (A1.9) the elastic modulus in the y direction can be expressed as

$$E_y = (k_{1n} \cos^2 \alpha) \frac{a}{b} + \left[\frac{m+1}{m} + \frac{n-1}{n} \right] k_{2n} \frac{a}{b} \quad (\text{A1.10})$$

A2. Shear stiffness

The effect of bonded and non-bonded interactions under shear conditions could also be described by a simple analytic model. Fig. A2.1. depicts a simple representation of CNC with the inter-plane and in-plane springs, shown in red and green color respectively. Three simple shear tests are considered: (1) shear on the yz-plane and parallel to y-direction called $shear_{xy}$, Fig. A2.1a (2) shear on the yz-plane and parallel to z-direction called $shear_{xz}$, Fig. A2.1(b), and (3) shear on the xz-plane and parallel to z-direction called $shear_{yz}$ (Fig. A2.1(c)). A model for in plane shear stiffness, $shear_{xy}$, is shown in Fig. A2.1(a). For these cases, the force-displacement relationship can be obtained using energy approach by equating internal and external energy as shown below.

$$U = 0.5 \times (k_{1n} L \cos^2 \alpha) \left(\frac{\delta}{2n} \right)^2 \times n \times m \times 4 = 0.5 F \delta \quad (\text{A2.1})$$

$$\tau_x = \frac{F}{WL}, \quad \gamma_x = \frac{\delta}{h}, \quad G_x = \frac{\tau_x}{\gamma_x} \quad (\text{A2.2})$$

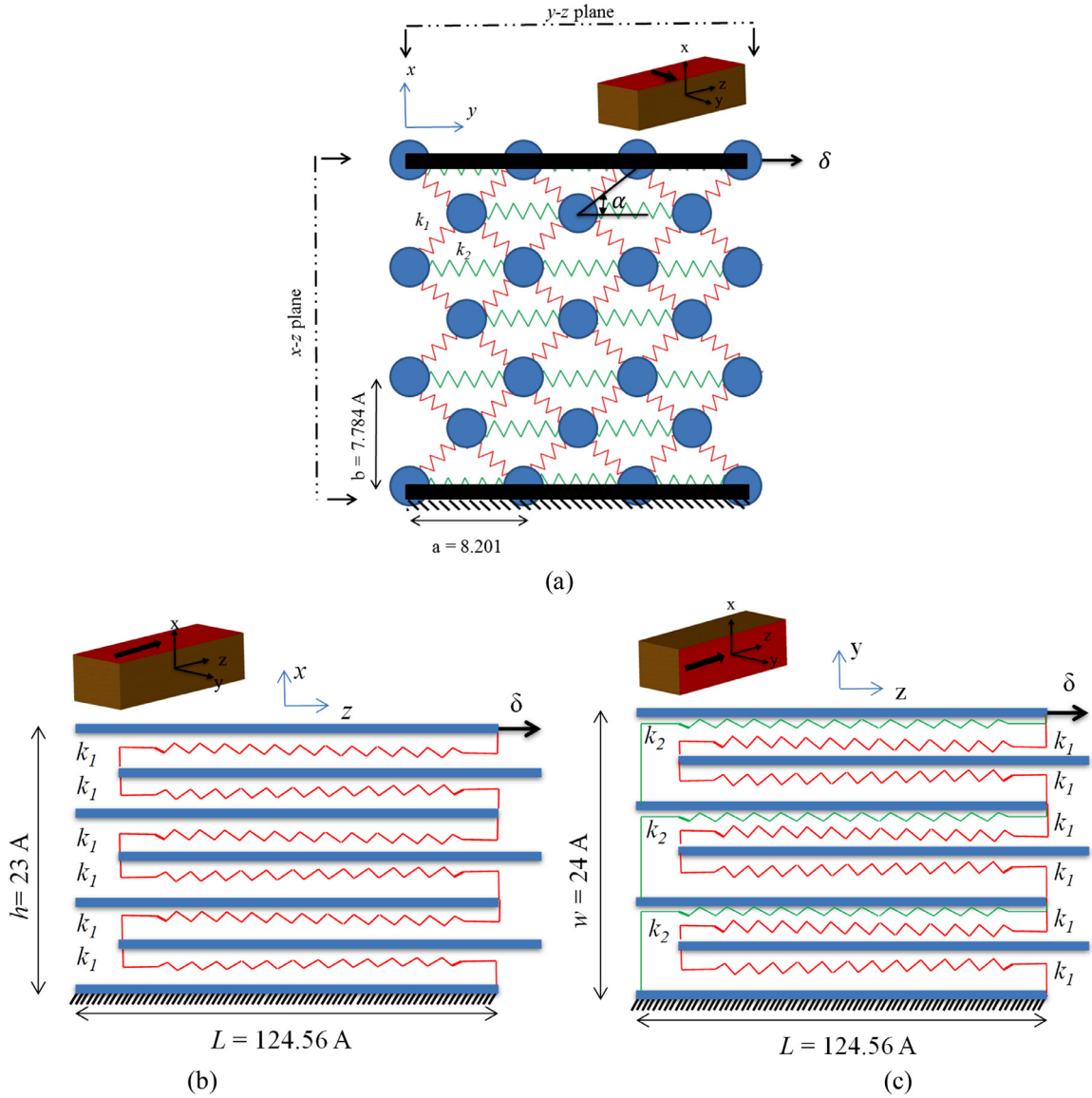


Fig. A2.1. Simplified representation of the cellulose crystal to evaluate the elastic shear behavior: (a) Each cellulose chain is shown with blue circle, the inter-plane stiffness is represented by red springs and the in-plane stiffness by green springs in 3×3 crystal (b) $shear_{xz}$ model with red spring representing the inter-plane VdW forces (c) $shear_{yz}$ model where red springs represent inter-plane stiffness and green springs show the in-plane stiffness. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article).

Where U is the internal energy, F is the external force, δ is the external displacement and $(\frac{\delta}{2n})$ is the deformation of each red spring in the x direction. By replacing F from Eq. (A2.1) and substituting $w = m \times a$, $h = n \times b$ into Eq. (A2.2) the elastic shear modulus becomes

$$G_{xy} = (k_{1n} \cos^2 \alpha) \frac{b}{a} \quad (A2.3)$$

For the second case, $shear_{xz}$, this relationship is defined based on k_1 which is the stiffness per length for inter-plane VdW forces and L , which is the length of the 3×3 crystal.

$$U = 0.5 \times (k_{1t} L) \left(\frac{\delta}{2m} \right)^2 \times n \times m \times 4 = 0.5 F \delta \quad (A2.4)$$

In Eq. (A2.4) $(\frac{\delta}{2m})$ is the displacement of each spring and $n \times m \times 4$ are the total number of springs

While for the $shear_{xz}$ case only inter-layer VdW forces are involved in shear, both inter-plane and in-plane stiffness contribute to shear for the $shear_{yz}$ case. Finally, for the third case, $shear_{yz}$, the force-displacement relationship can be obtained

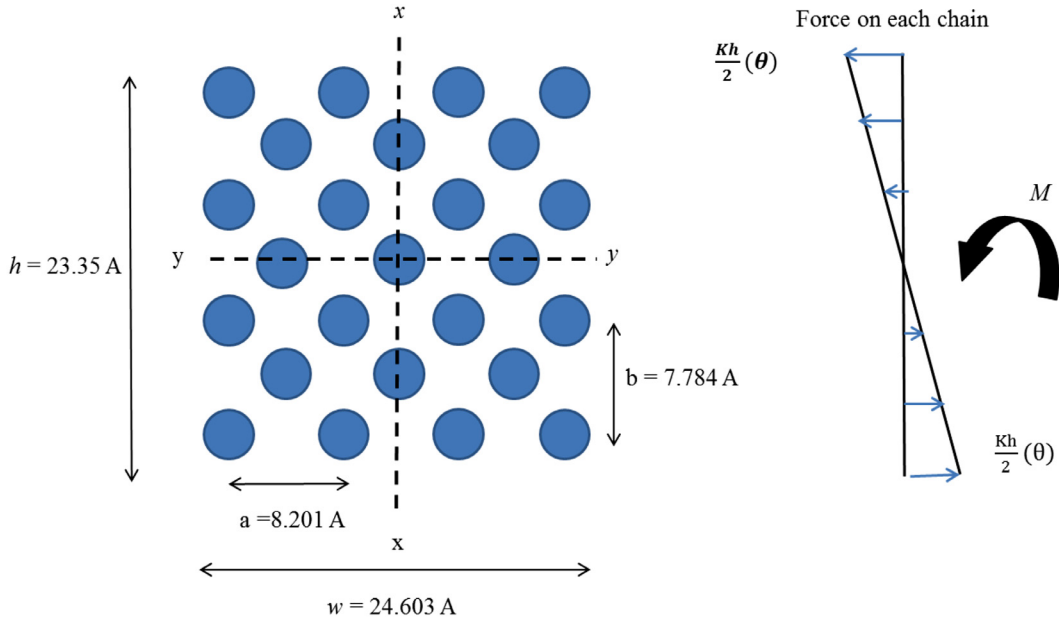


Fig. A3.1. Each cellulose chain is shown with blue circle in 3×3 crystal. Tension, compression forces induced at cross section due to bending of crystal. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article).

as follow:

$$U = 0.5 \times (k_{1t}L) \left(\frac{\delta}{2n} \right)^2 \times n \times m \times 4 + 0.5 \times (k_{2t}L) \left(\frac{\delta}{n} \right)^2 \times [n \times (m+1) + (n-1) \times m] = 0.5F\delta \quad (\text{A2.5})$$

Where k_1 and k_2 are the inter-plane and in-plane stiffness per length respectively. The shear modulus of CNC can also be obtained from these analyses as follow and using Eq. (A2.4) and Eq. (A2.5):

$$G_{xz} = \frac{Fh}{Lw\delta} = \frac{k_{1t}b}{a} \quad (\text{A2.3})$$

$$G_{yz} = \frac{Fw}{Lh\delta} = \left[k_{1t} + \left(\frac{m+1}{m} + \frac{n-1}{n} \right) k_{2t} \right] \frac{a}{b} \quad (\text{A2.4})$$

A3. Bending stiffness

We also developed a simple analytical model for a CNC under bending assuming that the bending stiffness is only governed by the stiffness of the individual chains and ignoring the non-bonded interactions to show the contribution of chain stiffness on bending stiffness. Fig. A3.1 represents the cross section of a 3×3 crystalline cellulose under bending replacing chains with blue circles. Although the cross section of CNC after equilibrium is not a perfect rectangular shape, we assume a rectangular shape for simplicity. Fig. A3.1(b) shows the applied bending moment, M , rotation angle, θ , height of the cross section, h , and resulting tension, compression forces applied to the chains.

The relationship between moment and bending radius per length at any cross section can be expressed as

$$M = 4 \left(\frac{kh^2}{2} \theta \right) + 3 \left(\frac{2kh^2}{9} \theta \right) + 4 \left(\frac{kh^2}{18} \theta \right), \quad k = \frac{EA}{L} \quad (\text{A3.1})$$

$$M = \frac{26h^2EA}{9} \left(\frac{\theta}{L} \right) \quad (\text{A3.2})$$

Where θ is bending angle, EA is stiffness of each chain, h is the height of the cross section and L is the length of each chain. By replacing EA from Eq. (A1.5), and considering $w = m \times a$, $h = n \times b$ and $m = n = 3$, the moment-curvature relationship from Eq. (A3.2) can be rewritten as:

$$M = \frac{26h^2}{9} \left(\frac{E_zwh}{N} \right) \left(\frac{\theta}{L} \right) = \frac{26}{25 \times 9} E_zwh^3 \left(\frac{\theta}{L} \right) \quad (\text{A3.3})$$

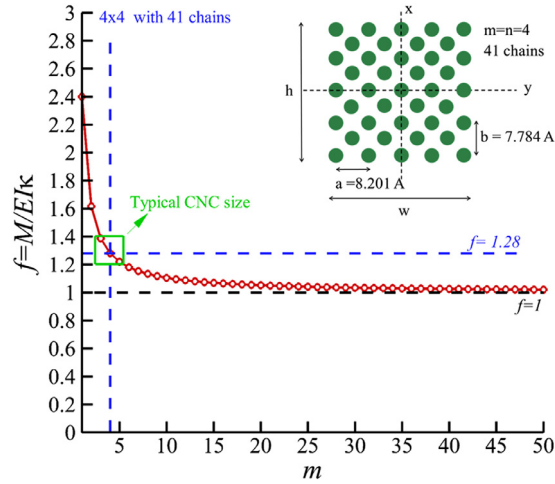


Fig. A3.2. Bending stiffness multiplier, f , for different size of CNC is plotted. The value of f for typical CNC size is 1.2–1.4 with average of 1.28 for $m=4$ with 41 chains.

Eq. (A3.3) can be further reduced considering the second moment of inertia of solids, $I = \frac{1}{12}wh^3$, and curvature $\kappa = \frac{\theta}{L}$

$$M \cong f \cdot E_z I \kappa \quad (\text{A3.4})$$

where for this particular case $f=4/3$. This general expression is similar to that obtained for isotropic solids (e.g., $M=EI\kappa$) expect that $f=1$. If we follow the same procedure for a crystal size of $m \times n$, the general relationship is obtained as follow:

$$M = \left[\sum_{i=0}^{\frac{n}{2}} 0.5(m+1) \left(\frac{n-2i}{n} \right)^2 + \sum_{i=1}^{\frac{(n+1)}{2}} 0.5m \left(\frac{n-2i+1}{n} \right)^2 \right] EAh^2 \left(\frac{\theta}{L} \right) \quad (\text{A3.5})$$

By replacing EA from Eq. (A1.5) and the second moment of inertia of solids, $I = \frac{1}{12}wh^3$, in Eq. (A3.5) the following expression is obtained.

$$M = 12 \times \left[\sum_{i=0}^{\frac{n}{2}} 0.5(m+1) \left(\frac{n-2i}{n} \right)^2 + \sum_{i=1}^{\frac{(n+1)}{2}} 0.5m \left(\frac{n-2i+1}{n} \right)^2 \right] \frac{E_z I}{(m+1)(n+1) + mn} \kappa \quad (\text{A3.6})$$

Leading to an expression similar to A3-4, except that the new coefficient f can be obtained by dividing Eq. (A3.6) by $El\kappa$. The values for coefficient for a square shape ($n=m$) with different values of m are plotted in Fig. A3.2. The coefficient value merges to 1, similar to solids, as the dimension increases and has the highest value of 2.4 for $m=n=1$. The value of f for typical CNC size is 1.214 with average of 1.28 for $m=4$ with 41 chains.

A4. Mesh sensitivity analysis

Although all the constitutive relationships in our continuum model consider that the individual cellulose chains are linear elastic infinitesimal strain conditions, local nonlinear deformations may cause mesh dependency associated with the beam element size. To further evaluate our model, we performed a convergence analysis on a 3×3 and 24 glucose rings long CNC (such as the one shown in Fig. 1(a)) subjected to tensile, bending, torsion and shear loading. In our analysis we replaced each chain with 1, 3, 6, 12 and 24 elements (associated with 24, 8, 4, 2 and 1 ring(s) per element, respectively). Fig. A4.1.(a) and (b) display the stress-strain curves for mesh sensitivity analysis of a tensile test performed along the longitudinal chain direction (green arrow in Fig. 6(a)) and Shear_{xz} test (red arrow in Fig. 6(b)) as explained in Section. 4. The results indicate no mesh sensitivity for tensile and shear test and the same curves are obtained from all the different mesh sizes.

Fig. A4.2.(a) and (b) display the moment-curvature curves for mesh sensitivity analysis of bending test parallel to the h -bond plane (red arrow in Fig. 6(a)) and torsion test (blue arrow in Fig. 6(a)) as explained in Section 4. For both, bending and torsion tests, the results for $L=1, 2$ and 4 ring(s) converge to the same value with negligible difference for $L=8$ and 24 ring(s) (18 and 5 nN.nm²/rad for bending and torsion tests respectively). We note that, for the deformation of individual chains in the system, adding more molecular units per element do not necessarily affect the deformation. This is because we are employing 3D Euler–Bernoulli beam element which provides 6-degrees of freedom per node. It is worth mentioning that even for CNCs under bending deformation, the chains are mainly under tension (chains below y - y axis in Fig. A3.1) or compression (chains above y - y axis in Fig. A3.1) and the results are independent of bending stiffness (EI) of chains as discussed in Section A3. Therefore, for bending, tensile and shear tests, where EI of the chains are not concerned, the results

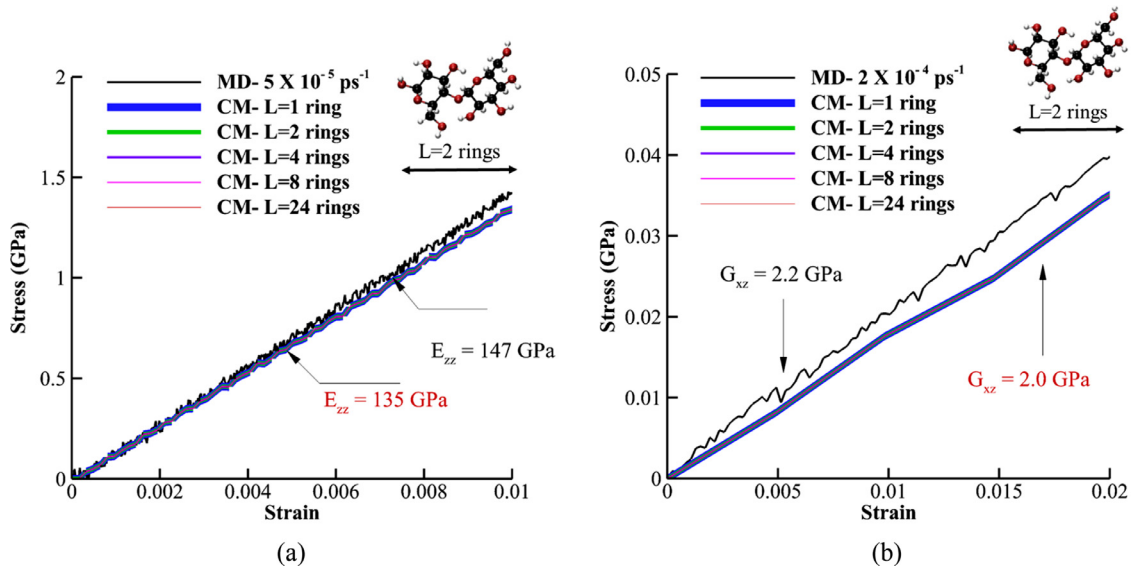


Fig. A4.1. Stress-strain curves from CM and MD for mesh sensitivity analysis of CNC with 1, 2, 4, 8 and 24 ring(s) per element size (L). (a) Tension applied along the longitudinal chain direction (b) Shear_{xz} test.

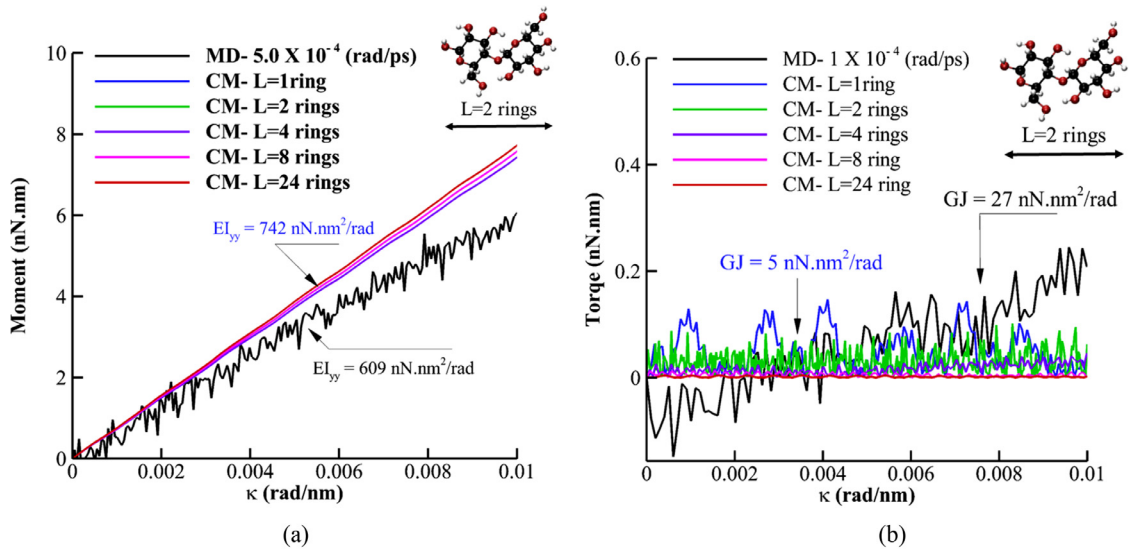


Fig. A4.2. Moment-curvature curves from CM and MD for mesh sensitivity analysis of CNC with 1, 2, 4, 8 and 24 ring(s) per element size (L). (a) Bending parallel to the h-bond plane reproduced from Fig. 9(a). (b) Torsion test reproduced from Fig. 10 (a).

are independent of the mesh size. For the torsion test, although the CNC is under torsion, the chains experience out of plane bending deformation; therefore EI of chains, and consequently the element size, become more important. However, since the torsional stiffness (GJ) of CNC is very small, especially in comparison with EI , we can still employ a very coarse mesh without introducing significant variations in the results. For example, for $L=24$ rings $GJ=0.0$ nN.nm²/rad and $EI=760$ nN.nm²/rad while for $L=1,2$ and 4 ring(s) the results converge to $GJ=5$ nN.nm²/rad and $EI=742$ nN.nm²/rad with 18 and 5 nN.nm²/rad for bending and torsion tests, respectively.

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