Multiscale Modeling of the Hierarchical Structure of Cellulose Nanocrystals

Abstract. *A multiscale framework is being developed to predict and describe the thermomechanical behavior of cellulose nanocrystals using state-of-the-art computational tools capable of connecting atomistic-based simulations to experiments through continuum-based modeling techniques. As part of our efforts, we began our investigation at the atomistic level using first-principle theories and molecular dynamics simulations to extract key mechanical properties (axial, bending, and torsional stiffness) for isolated cellulose chains and single crystals as well as the thermal conductivity coefficients. A new continuum theory was developed to simulate cellulose nanocrystals using the finite element method.*

Keywords. Crystalline cellulose, hydrogen bonding, multiscale modeling.

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Introduction. The goal of this work is to develop a multiscale framework that will enable us to generate a model that is capable of reproducing the behavior of cellulose nanocrystals (CNCs) and that can be extended to any material with similar characteristics such as other polysaccharides (e.g., α-chitin). To understand the internal behavior of CNC, it is necessary to comprehend the role of bonded interactions (covalent bonds) and non-bonded interactions (van der Waals, hydrogen bonds, Coulomb) in mechanical and thermal properties, as well as any other internal processes that can define the behavior of the entire system (Fig. 1). The present work is based on the hypothesis that bonded and non-bonded interactions can be decoupled. Bonded interactions determine cellulose-chain behavior, whereas non-bonded interactions define inter-chain behavior (e.g., crystal size and lattice parameters). The response of the crystal as a whole arises from the mutual action of these two mechanisms.

Methodology. The computational approach selected here uses a multiscale strategy to model the behavior of indi-
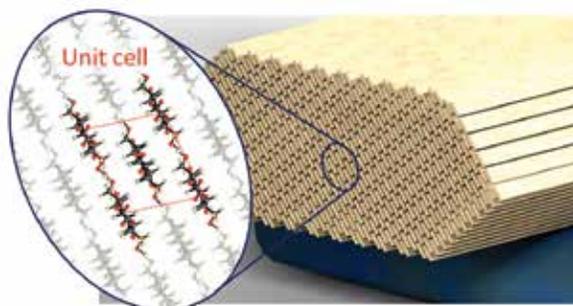

Figure 1. *Schematic representation of a CNC modeled using continuum theory. At this level, each cellulose chain is treated as a beam element, and the system is linked together by non-bonded interactions (omitted for clarity)*

vidual CNCs and CNC-based materials, connecting first-principle calculations of CNCs to continuum models for CNC-based composite materials. Figure 2 depicts a summary of tools and approaches used in the current study. At the nanoscale, we perform explicit atomistic simulations to test our initial hypothesis and to progress towards a complete understanding of the physics involved in the behavior of CNCs. Abinitio modeling techniques like quantum mechanics and density functional theory (QM-DFT) or quantum chemistry can be used to model atom-by-atom interactions in the most comprehensive way available today. Although QM-DFT enables us to simulate hundreds of atoms on a picosecond timescale, molecular dynamics (MD) is capable of simulating times up to microseconds with millions of atoms involved. This is achieved by reducing the details involved in each atomic interaction. With today's computational power, it is possible to simulate the behavior of an entire CNC crystal using MD.

However, the interaction between large CNCs and the behavior of the crystal as reinforcement material are still out of the reach of molecular dynamics simulation. Coarse-grained continuum mesoscale theories emerge as a possible solution to studying the fundamental mechanical interaction of larger systems. Continuum models do not consider atomic interactions in the same way that QM and MD do. Instead, the entire system (e.g., individual molecular chains or entire CNCs) can be treated as a whole and not as a group of individual atoms. Increasing the size and time length of the system is achieved
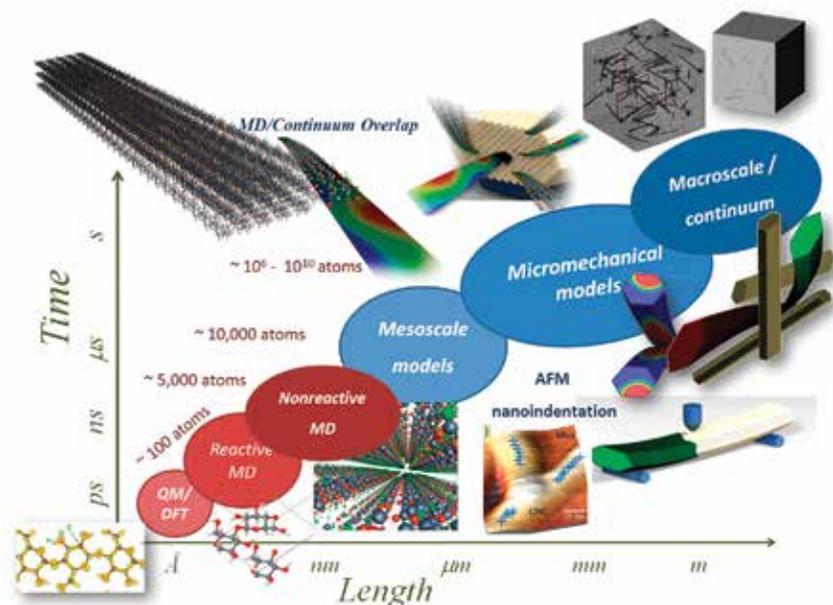
Figure 2. Time-length scale map. In red, techniques that take into account atoms in an explicit way; in blue, "continuum" theories.
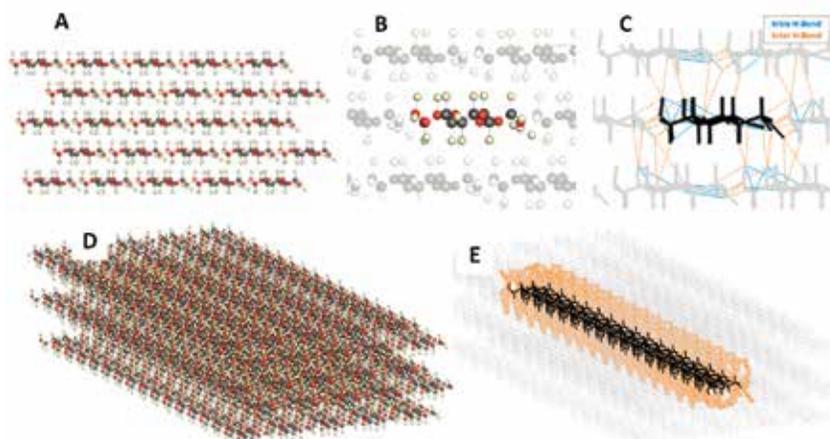

Figure 3. (A) 2D atomistic representation of a CNC. (B) Isolation of a single cellulose chain inside the crystal. (C) Schematic representation of all possible H-bond interactions for a given chain. (D) 3D atomistic representation of a CNC. (E) Schematic representation of the inter-chain H-bonds of an interior chain. The number of H-bonds formed depends on the force-field parameterization. Figures are only for illustration purposes.

by reducing the detail involved in each length scale. For instance, when going from MD to a continuum representation of cellulose chains, the results will depend greatly on the force-field parameterization used to run the simulations. Keeping in mind these limitations, continuum theory has the advantage of simulating large systems that are far beyond the reach of MD. The key is capturing the right physics at each length and time scale to feed the next scale with the right parameters. In our approach, we are not trying to fit variables to match simulations and experi-ments. The main goal is to connect several length scales, accounting for the necessary mechanics and physics involved at each scale, to capture the right macroscopic behavior that ultimately can be compared with experiments.

Results. Our preliminary study using molecular dynamics demonstrated that simple continuum-based beam theory could indeed be used to simulate cellulose chains in a finite-element framework. However, the non-bonded interaction needed additional development. As such, we
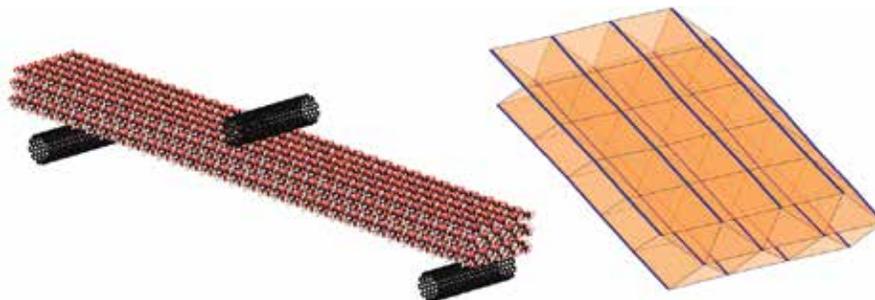
Figure 4. *Three-point bending configuration (left) to extract mechanical properties of CNCs using MD simulations (right). Continuum model of cellulose nanocrystals. Each single chain is represented by a specially designed beam element (blue); non-bonded interactions are captured by a homemade "hydrogen-bond element" (orange). Note that the beam elements are not originally straight and that the crystal is free to twist as it was observed in MD simulations.*

developed special hydrogen bonds and wan der Waals interaction elements that can be integrated with the beam elements that representing the individual CNC chains. Figure 3 shows some details of the hydrogen-bond elements. To characterize and validate these new non-bonded theories, thought experiments borrowed from fracture mechanics were used to set up several MD simulations. A modified version of LAMMPS[4] coupled with a ReaFF force field was used in all the simulations discussed in this work. Two main groups of simulations were conducted, the first set consists of single chains of different lengths, whereas the second involves crystals of various sizes.
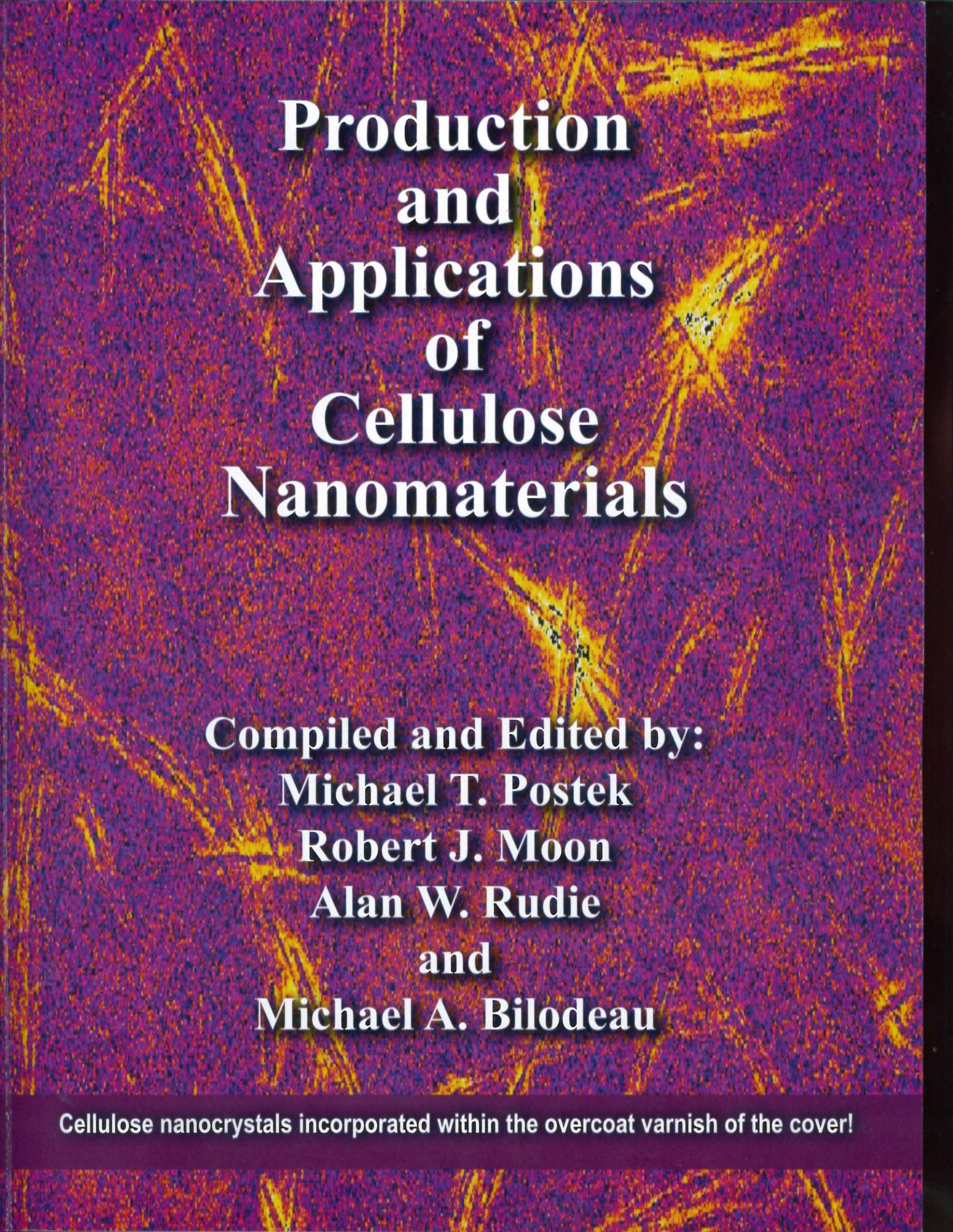
All the previous results were used to construct a continuum model. Single-chain simulations provided four key stiffness parameters that were used to feed our continuum beam model for cellulose chains. Single crystal molecular dynamics and quantum mechanics simulations provided insight into the non-bonded interactions (van der Waals, hydrogen bonds, Coulomb) that enabled us to fine our hydrogen-bond element. Overall, the two continuum elements working together made it possible to model fully a cellulose nanocrystal using continuum theory.

Conclusions. A comprehensive solution to modeling cellulose nanocrystals from a continuum point of view was presented. Continuous theory can be applied to molecular systems under certain conditions but not without special care. The next step in our work is to simulate three-point bending (Fig. 4) and nano-indentation experiments to correlate our models with experimental data. For more information on our current work see [5, 6].

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Production and Applications of Cellulose Nanomaterials

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Cellulose nanocrystals incorporated within the overcoat varnish of the cover!

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