Crystalline Cellulose – Atomistic Modeling Toolkit

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★ Introduction

Cellulose nanocrystals (CNCs) [1] are particles that can be extracted from wood and provide a unique "building block" on which a new biopolymer composites industry can be based.

CNCs have unique mechanical, photonic, electrical, and thermal properties, providing the opportunity to produce a new generation of green nanocomposites with wide ranging applications from packaging to flexible solar panels.

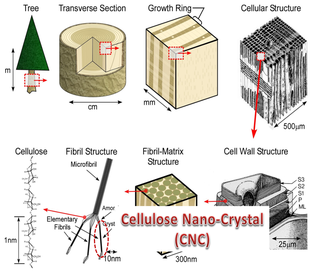

Fig. 1. From Moon et al., Chem Soc Rev 2011 shows the wood structure, i.e. Hierarchy of cellulose.

How do CNC look like? And How big are they?

Isolated CNs

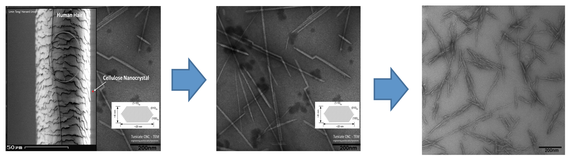

Fig. 2. Tunicate CNC - TEM (engineering.purdue.edu/nanotrees)

★ Objectives

- **Predict mechanical properties of individual CNC**
  - ✓ Elastic behavior
  - ✓ Inelastic behavior
  - ✓ Strength
- **Characterize and predict:**
  - ✓ CNC/CNC interaction (adhesion)
  - ✓ CNC/Matrix interaction
- **CN-based materials**
  - ✓ Inelastic behavior
  - ✓ Strength and Toughness
  - ✓ Others (e.g, CTE)
- **Design new materials**

High Elasticity & Strength:

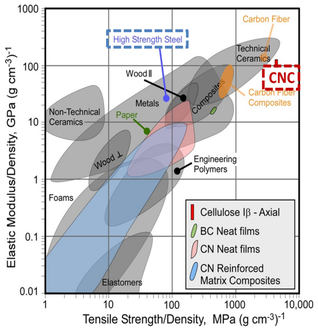

Fig. 3. From Moon et al., Chem Soc Rev 2011. High elasticity and Strength.

Transparent:

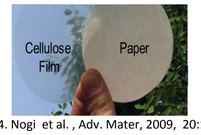

Fig. 4. Nogi et al. , Adv. Mater, 2009, 20:1-4.

Low Thermal Expansion:

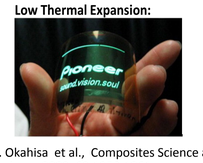

Fig. 5. Okahisa et al., Composites Science and Technology, 2009, 69:1958-1961.

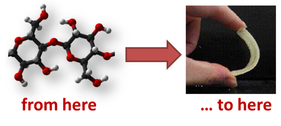

Fig. 6. Winter, William T., Ecocomposites Reinforced with Cellulose Nanoparticles: An Alternative to Existing Petroleum Based Polymer Composites

- Develop a nanoHUB [2] atomistic simulation toolkit capable of running molecular dynamic simulations to study the nonlinear structural behavior of cellulose chains and their interactions in crystalline cellulose.

★ Acknowledgements

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★ Methodology

Cellulose is an organic compound formed by Carbon, Hydrogen and Oxygen ions $(C_6H_{10}O_5)_n$, arranged in linear chains of several hundred to over ten thousand β(1→4) linked D-glucose units [3].

A C program capable of generating CNCs based on Nishiyama et al. [3] coordinates was used to populate the initial atomic positions. Different sizes and shapes, ranging from single chains to fully sized crystals, can be created by the user with a simple but very powerful graphical user interface.

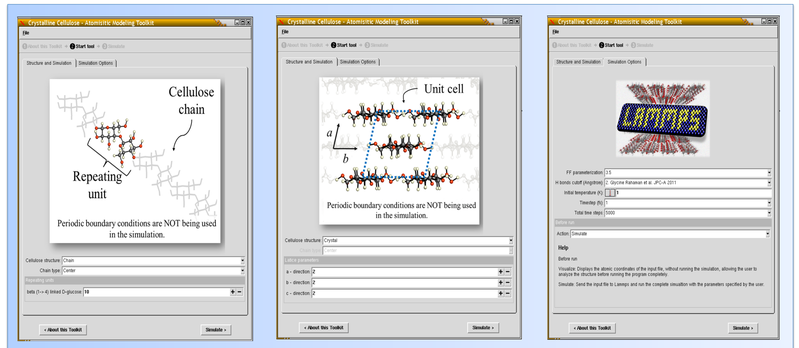


Fig. 7. Crystalline Cellulose – Atomistic Modeling Toolkit. Inputs: lattice parameters and simulation options

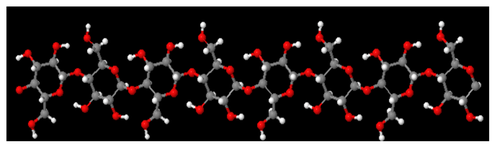


Fig. 8. Single cellulose chain formed by 8 glucose rings according to Nishiyama et al [3] atomic coordinates.

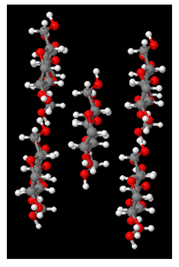


Fig. 9. Unit cell structure of the cellulose I_β network A [3] showing the characteristic layered conformation

Molecular dynamic simulations are performed by LAMMPS [5] coupled with ReaxFF force field [6]. The system is equilibrated in a NVT ensemble (constant number of atoms, volume and temperature) with a total simulation time and temperature defined by the user. Periodic boundary condition are not applied to any of the simulations.

Several simulation parameters can be defined, such as: temperature, time step, total number of steps, hydrogen bond cutoff distance and force field parameterization.

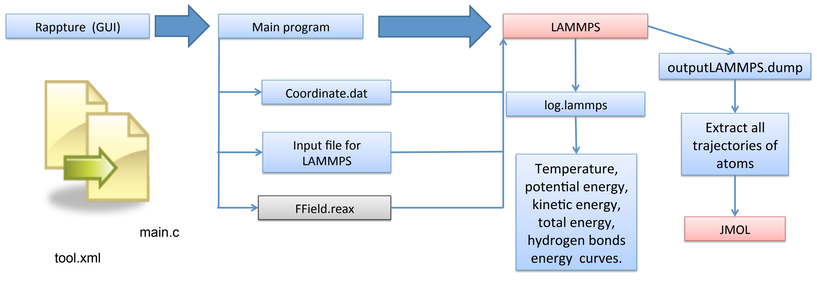


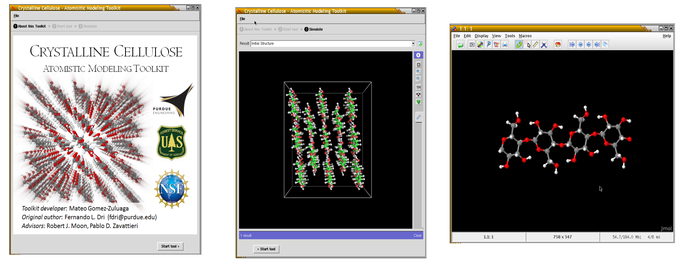
Fig. 10. Flowchart of the nanoHUB tool [2]. The main program generates the necessary files according to user preferences. LAMMPS [6] is used to run the atomistic simulation. JMOL is used for trajectory visualization.

★ Results

JMOL [7] is used to visualize atom displacements (trajectories) producing state-of-the-art interactive images of the simulation results. XY-plots of temperature, potential energy, kinetic energy, total energy and hydrogen bonds energy are being automatically generated to help understanding the thermodynamic evolution of the simulated system.

The next figures shows the final version of the tool and its outputs.

Crystalline Cellulose – Atomistic Modeling Toolkit



Outputs:

- 3D CNCs structure
- Atom trajectories (JMOL)
- LAMMPS log
  - Records commands and simulation history
- XY Plots
  - Temperature
  - Potential energy
  - Kinetic energy
  - Total energy
  - Hydrogen Bonds energy

Fig. 11. Crystalline Cellulose – Atomistic Modeling Toolkit. Cover and Outputs

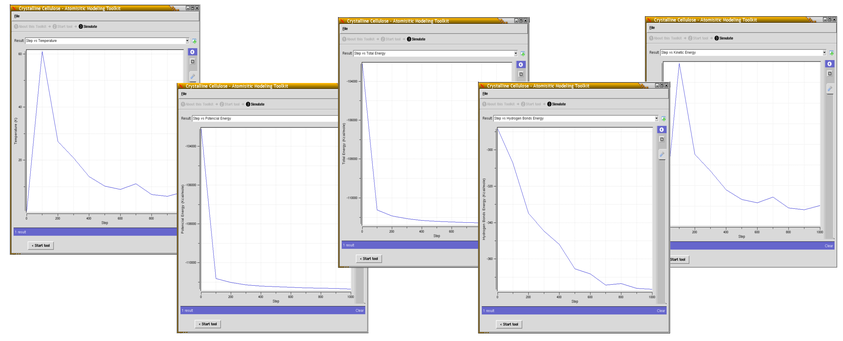


Fig. 12. Crystalline Cellulose – Atomistic Modeling Toolkit. Thermodynamic evolution of the simulated system

★ Conclusion and Future Work

A molecular dynamic simulation toolkit was created to analyze the mechanical response of crystalline cellulose ranging from a single cellulose chain to fully sized crystal. LAMMPS simulation code coupled with ReaxFF force field provides the necessary platform to run molecular dynamics simulations. JMOL viewer was incorporated into the toolkit to provide state-of-the-art images of the results.

Some of the future work includes:

- Parallelization to increase performance
- Extend the simulation capabilities
- Hydrogen bonds visualization
- Extension to similar system (i.e. alpha-chitin)

★ References

[1] Moon, R. J., Martini, A., Nairn, J., Simonsen, J., & Youngblood, J. (2011). *Cellulose nanomaterials review: structure, properties and nanocomposites. Chemical Society reviews* (Vol. 40, pp. 3941–94). doi:10.1039/c0cs00108b
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[7] Jmol: an open-source Java viewer for chemical structures in 3D. http://www.jmol.org/