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PREDICTING THE THERMAL PROPERTIES OF CELLULOSE NANOCRYSTAL USING MOLECULAR DYNAMICS

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ABSTRACT

The thermal conductivity of the I-β cellulose nanocrystal is one of the basic thermal physical properties which can affect its utilisation. The precise simulation of the temperature gradient of cellulose nanocrystal is the preliminary step for calculation of the thermal conductivity. In this study, both the non-equilibrium molecular dynamics and its reverse method are employed with different thermostatting methods. A triclinic box containing 4×4×8 unit cell is built with the β-D-glucose as the monomer structure of cellulose molecules. The simulation is performed under the ambient temperature and pressure. The reactive force field, *i.e*., ReaxFF is used. The exact temperature profile obtained indicates that the molecular dynamics simulation is a promising and capable method to calculate the thermal properties of cellulose nano crystal.

Keywords: cellulose nanocrystal, thermal property, modelling, molecular dynamics

1. INTRODUCTION

Biomass is the most abundant renewable energy resource available today. There is increased exploitation of biomass to provide food for an ever growing population and industry to develop novel products. However, in the face of climate change, pollution, and increased pressure on land and water resource, biomass has to be utilized efficiently to remain a sustainable resource. Biomass comprises mainly of three natural polymers, cellulose, hemicellulose, and lignin. The composition of polymers varies based on the type of biomass, physical properties, development conditions, composition of soil and growth climatic conditions [1].

Cellulose is a long linear chain like structure composed of (1,4) linked β-D glucopyranosyl units assembled into hierarchical structures of microfibrils. Cellulose occurs in two distinct, yet coexistent crystal phases, I-α and I-β. Plant-based microfibrils are believed to exist primarily in the I-β phase [2]. Nanocellulose refers to a cellulosic material whose dimension is in the range of 1 to 100 nm in at least one dimension obtained from various lignocellulosic fibres and bacteria [3]. Nanocellulose is synthesized via different treatment methods and can be broadly classified into cellulose nanocrystals (CNC), cellulose nanofibers (CNF) and bacterial nanocellulose (BNC). Bacterial nanocellulose will not be discussed further in this study. CNCs are rod-like shapes containing only crystalline domain while CNFs are web-shaped fibres stabilized by hydrogen bonds consisting of both crystalline and amorphous domains [1]. Nanocrystals prepared from plant celluloses have spindle-like morphologies with average widths and lengths of ∼15 and ∼150 nm, respectively [2]. The main sources of CNFs and CNCs are hard and soft wood, seed fibres, bast fibres, grasses and agricultural waste like bagasse.

Nanocellulose are ubiquitous, biodegradable, combustible, cost-effective, low weight, high flexibility, and have exceptional mechanical properties (high Young's modulus and high tensile strength), low coefficient of thermal expansion, and low abrasive nature [4, 5]. Nanocellulose has therefore been widely applied in construction, electronic, automotive, packaging, pharmaceutical and cosmetic industry owing to their mechanical properties. Nanocellulose have also

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been applied in the energy sector for energy conversion, storage devices, biocomposites and biofuels owing to their carbon storing capacity, good electric conductivity, biodegradability, biocompatibility, low cost and reduced toxicity among others [1, 6-10].

To diversify and broaden the application of nanocellulose, understanding the molecular behaviour of cellulose allomorphs is critical [1]. There are however significant experimental challenges in sample handling, thermal probing and characterizing cellulose which has a small diameter (5-30 nm) [11, 12]. Molecular dynamics (MD) is a computational method that can be employed to study nanocellulose at atomic level. There are several studies published on MD simulations investigating the structure and dynamics of nanocellulose using different force fields. However, most of these studies focus on the mechanical properties of nanocellulose. Pablo *et al*. [13] studied the thermo-mechanical properties of CNCs with evaluation of several different force fields, *e.g*., CHARMM-AA, GLYCAM, COMPASS and ReaxFF. Wu *et al*. [14, 15] predicted the elastic modulus and tensile strength of I-β CNCs with a relatively small model: ~5nm in the transverse directions and ~10 nm in the chain direction. Jairo *et al*. [16], Zhang *et al*. [17] and Malin *et al*. [18] studied the thermal response of I-β CNCs with the GLYCAM 06 force field, ReaxFF force field and GROMOS 45a4 force field, respectively. Jairo *et al*. [19] also studied the thermal conductivity of single CNCs and interfacial thermal resistance of CNC-CNC with ReaxFF force field. In their research, the calculated thermal conductivity of a single CNC is approximately 5.7 ± 0.9 $W \cdot m^{-1} \cdot K^{-1}$ in the chain direction and 0.72 ± 0.12 $W \cdot m^{-1} \cdot K^{-1}$ in the transverse direction using Fourier's law. However, the specific method used to obtain these results is not provided.

As the temperature profile can manifest the heat transfer property and is basic for the thermal conductivity calculation, this study therefore focuses on the temperature gradient of I-β cellulose CNC using non-equilibrium molecular dynamics (NEMD). Four methods, namely, direct thermostatting method using a langevin thermostat, and the reverse NEMD using heat-exchange (HEX) algorithm, enhanced heat exchange algorithm, *i.e*., eHEX algorithm and the Muller-Plathe [20] algorithm are used to determine the thermal profiles of the CNC.

2. SIMULATION METHODS

2.1 Crystalline cellulose model

In this research, a triclinic box of 4×4×8 I-β unit cell is constructed as shown in Fig 1. (a). The lattice parameters are a=0.7784 nm, b=0.8201 nm, c=1.038 nm, α=β=90°, γ=96.5°. The β-D-glucose is the monomer structure of cellulose molecules. The atomic conformation of cellulose monomer is shown in Fig 1. (d). Two identical β-D-glucose hydrocarbon groups linked each other and compose a unit of cellulose $[\beta\text{-D-glucose}]_n$. Carbon atoms are in six-membered ring of each glucose group, but they are not in the same plane. Being linked each other by common oxygen atom, glucose groups are polymerized into a large polymer.

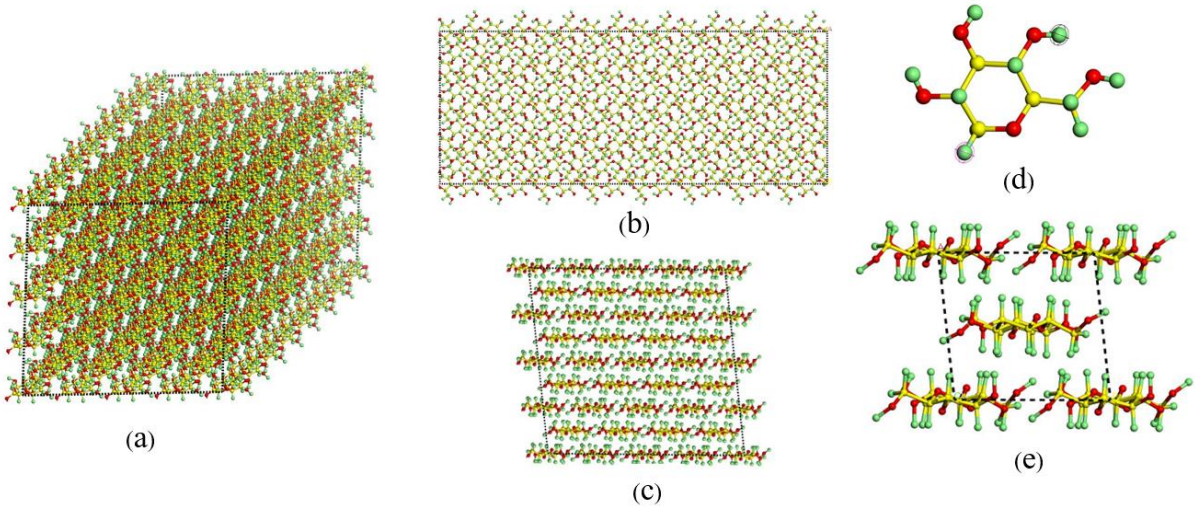

Fig 1 . (a) Perspective view of the triclinic box with 4×4×8 unit cell; (b) y-z plane of the triclinic box; (c) x-y of the triclinic box; (d) monomer structure of β-D-glucose with green spheres indicating the hydrogen atoms, red spheres indicating the oxygen atoms and the yellow spheres indicating the carbon atoms; (e) I-β unit cell with the lattice parameters that describe the cross section.

2.2 Simulation setup

All the simulations are performed in LAMMPS (Large-scale Atomic/Molecular Massively Parallel Simulator) package [21]. The system consists of 13892 atoms in a triclinic periodic box of size 44.7 Å ×36.8 Å ×87.5 Å. The time step is set as 0.1 fs which is small enough to capture the movement of hydrogen atom. Before the temperature gradient is calculated, three equilibrium runs are performed to minimize the system energy. The simulation is firstly performed under isobaric-isothermal (NPT) ensemble at 300K and 1bar for 10 ps with temperature damp 10 and pressure damp 100 before switching to isochoric-isothermal (NVT) ensemble and canonical ensemble (NVE). The final results are averaged over every 10000 steps.

3. RESULTS AND DISCUSSION

In order to calculate a temperature profile or impose a heat flux, the simulation box is divided into 20 slabs with identical thickness in the z direction as shown in Fig. 2. For the direct thermostatting method, two thermostats for two regions of simulation box with one hot side at 15-25 Å the other cold side at 55-65 Å are fixed by langevin thermostat. Then the flux of energy can be monitored to maintain the temperature gradient. In this study, the temperature of hot side is set as 330K and temperature at cold side is set as 270 K. The reverse NEMD with heat-exchange (HEX) algorithm, enhanced heat exchange algorithm, *i.e.*, eHEX algorithm and the Muller-Plathe [20] algorithm are used. The usual NEMD approach is to impose a temperature gradient on the system and measure the response as the resulting flux. In the reverse NEMD method, the heat flux is imposed, and the temperature gradient is the system's response. For HEX algorithm and the eHEX algorithm, temperature gradient is established across the simulation domain by adding energy to the hot region and subtracting energy from the cold reservoir. In this simulation, the rate of heat addition or subtraction is set as 0.1 Kcal·mol^{-1}·fs^{-1}. The eHEX algorithm is an extension of the heat exchange algorithm and adds an additional integration for higher-order truncation terms in the operator splitting. In

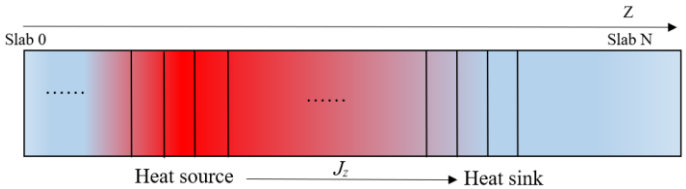

Fig 2. Schematic representation of the subdivided periodic simulation box.

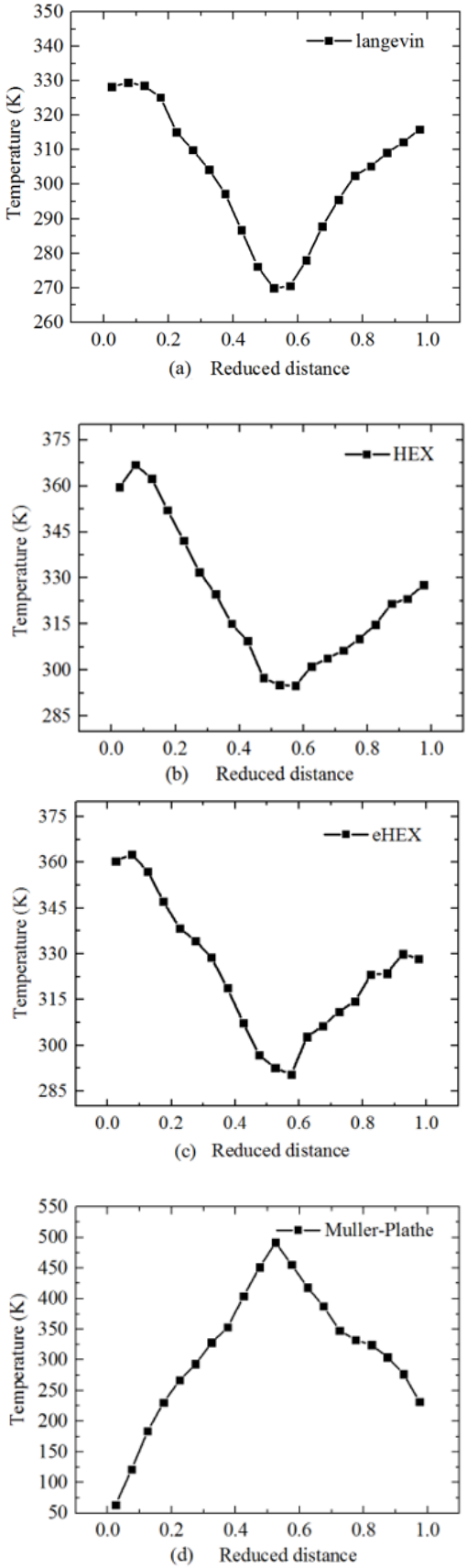

Fig 3. Temperature gradient with ReaxFF force field and different methods.

Muller-Plathe method, the hottest atom in cold region and the coldest atom in the hot region would be found and the velocity vectors of these two atoms are swapped. Then the heat flux due to the kinetic exchange is tallied and the induced temperature profile monitored. The temperature profiles from the different methods shown in Figure 3 can be used to calculate the thermal conductivity of the cellulose nanocrystal.

4. CONCLUSIONS

In this study, non-equilibrium molecular dynamics and its reverse method are used to simulate the temperature profile of cellulose nanocrystal under the ambient temperature and pressure. The direct non-equilibrium method with langevin thermostatting can fix the temperature precisely at the hot and cold slab and produce a temperature gradient in the intermediate. The exact temperature response of the reverse non-equilibrium with imposed heat flux also manifests that the reactive force field and the current simulation setup are capable for calculation of thermal conductivity quantitively.

In the future research, both the equilibrium molecular dynamics with Green-Kubo equation and the non-equilibrium with Fourier equation will be taken into consideration to calculate the thermal conductivity. Moreover, the coarse grain method will be used to extend the length of cellulose nanocrystal to fibrous scale.

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