

Multiscale coarse-grain simulation studies of cellulosic biomass

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Understanding cellulose structure and dynamics is important for improving the process of conversion of biomass to ethanol. Here, we explore cellulose fibril structure, dynamics, and degradation pathways by developing multiscale methods for extending the time and length scales accessible to biomolecular simulation on massively parallel supercomputers. For this purpose, high-level quantum mechanics calculations are performed by using the fragment molecular orbital (FMO) method in GAMESS (General Atomic and Molecular Electronic Structure System). The FMO simulations are used to study the relevant catalyzed reaction paths, with the solvent represented by the effective fragment potential (EFP) method. The combined FMO/EFP methods are used with molecular dynamic simulations to provide coarse-grained (CG) potentials using the force matching method.

Further, accurate parameterization of glucose monomers derived from quantum mechanical calculations is used as input for classical molecular dynamics (MD), which in turn is utilized to develop a large-scale CG force field for the cellulose fibril. Using distribution functions from atomistic MD simulations as target observables, we developed a single bead per monomer CG model for cellulose fibrils that is found to be able to reproduce structural features of crystalline cellulose. Without the use of constraints the CG crystalline fibril remains stable over the maximum simulation length explored in this study ($>1 \mu\text{s}$). We also extend the CG representation to model fully amorphous cellulose fibrils. This is done by using an atomistic MD simulation of fully solvated individual cellulose chains as a target for developing the corresponding fully amorphous CG force field. Fibril structures with different degrees of crystallinity are obtained using force fields derived using a coupling parameter that combines the crystalline and amorphous potentials (Figure 1). The method provides an accurate and constraint-free approach to derive CG models for cellulose with a wide range of crystallinity, suitable for incorporation into large-scale models of lignocellulosic biomass.

Furthermore, we have studied the cellulose fibril using the REACH (Realistic Extension Algorithm via Covariance Hessian) CG method. The underlying principle of REACH, a CG approach recently developed in our laboratory, is to obtain, from atomistic simulations, information on correlated motion and then use it to construct CG simulation models. The method is, in principle, a direct mapping of the atomistic force field onto the CG model without the need of iterative optimization. Our application of REACH to the cellulose I_{β} fiber shows that the REACH force field reproduces harmonic fluctuations from all-atom simulation and the computed longitudinal Young's modulus (~ 320 GPa) qualitatively compares to the experimental measurements (120–220 GPa). Together these simulation results contribute to our understanding of biomass recalcitrance to hydrolysis.

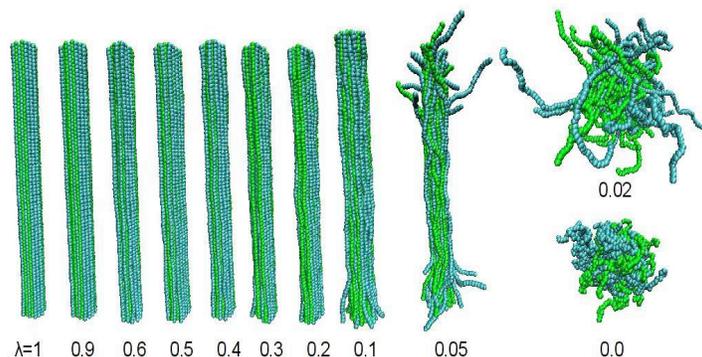


Figure 1. Final snapshots of CG cellulose fibrils with different λ values.