A Multiscale Approach to the Simulation of Lignocellulosic Biomass

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The present research involves the development of multiscale simulation methods and their application to solve critical problems needed for overcoming the recalcitrance to hydrolysis of lignocellulosic biomass, which is the bottleneck in cellulosic ethanol production. The multiscale methodologies span from accurate quantum-chemical techniques, needed to understand critical local interactions in biomass, to atomistic and coarse-grained simulations, needed to approach systems-level phenomena.

Quantum mechanics (QM) provides the fundamental framework for understanding chemical reaction processes. To reveal the local point interactions in biomass we apply the fragment molecular orbital (FMO) method, which divides a molecular system into fragments, in such a way that the near-field interactions of each fragment are treated with the full QM method (e.g. second order perturbation theory), while the far-field interactions are represented by electrostatic potentials. This approach leads to considerable computational time savings, and so enables simulations of large systems. FMO was adapted for polysaccharides and has been shown to give accuracy closely approaching that of the corresponding QM calculations. The accurate representation of solvent effects is vital to simulate the processes in solution, and in this research multi-layer methods are used for this purpose. The inner layer is the biomass complex represented by the QM method. The second (inner solvent layer) is represented by effective fragment potentials (EFP), which have been shown to provide a very accurate representation of intermolecular interactions. The outermost layer is represented by the implicit polarizable continuum method. The high level FMO-based QM methods in combination with the above solvent model have been applied to study key bond energies and thermodynamic properties in cellulose.

Seamless interfaces have been created between the above methods with simpler model potentials that retain the essential physics while allowing systems-level simulation of biomass properties. A force-matching model originally proposed by Voth and co-workers was applied to coarse grain the intermolecular potentials obtained using QM methods. In the force-matching scheme, pairwise forces between coarse-grain (CG) sites are mapped, using least-squares optimization, to a set of reference forces derived from *ab initio* or atomistic molecular dynamics (MD). An essential feature of the coarse-graining approaches used here is to start with relatively short-time MD using the FMO of EFP method. This provides the forces to be matched for the fully atomistic model potential. The CG potentials are then used for coarse-grained MD simulations on water solution of sugars, which is an intermediate step in ethanol production.