

Simulation Analysis of the Temperature Dependence of Lignin Structure and Dynamics

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Background

- Lignin is a key source of the recalcitrance of biomass to hydrolysis because it aggregates and precipitates onto cellulose after high temperature pretreatment of biomass in industrial biofuel production. Therefore, the temperature dependence of lignin structure is of interest as it is closely related to the effects of pretreatment. Furthermore, the molecular-level origin of lignin hydrophobicity, which is directly related to its biological function, was unknown.

Findings

- Extensive molecular dynamics simulation reveal that, with increasing temperature, lignin transitions from glassy, compact to mobile, extended states at $T \geq 150^\circ\text{C}$ i.e., above typical pretreatment temperatures. The hydrophobic collapse of lignin polymers is found to be thermodynamically driven by the increase of the translational entropy and density fluctuations of water molecules removed from the lignin surface.

Impact

- Simulations suggest lignin aggregation occurs during the heating phase of pretreatment, not during cool-down as was previously assumed. Implications beyond lignin include the thermodynamic role of water density fluctuations in hydrophobic polymer collapse.

