Computer Simulation of Lignocellulosic Biomass

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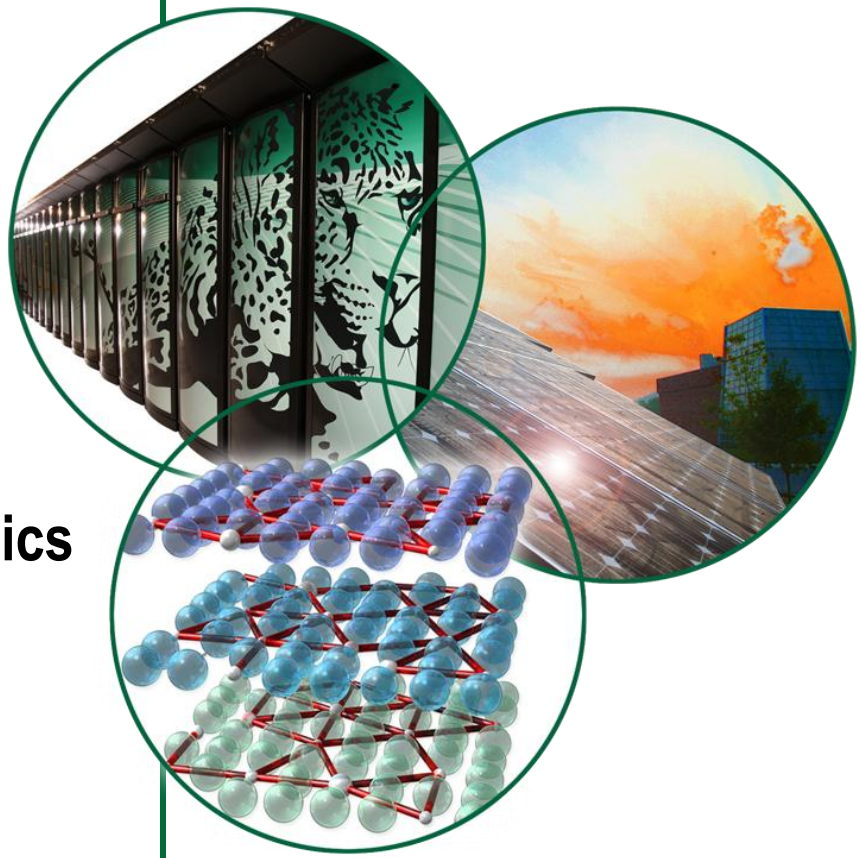

U.S. DEPARTMENT OF ENERGY

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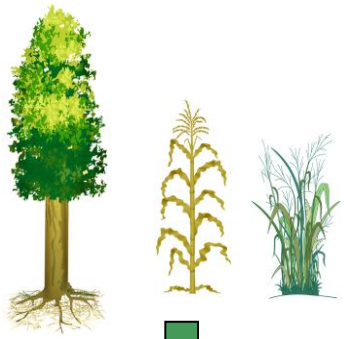
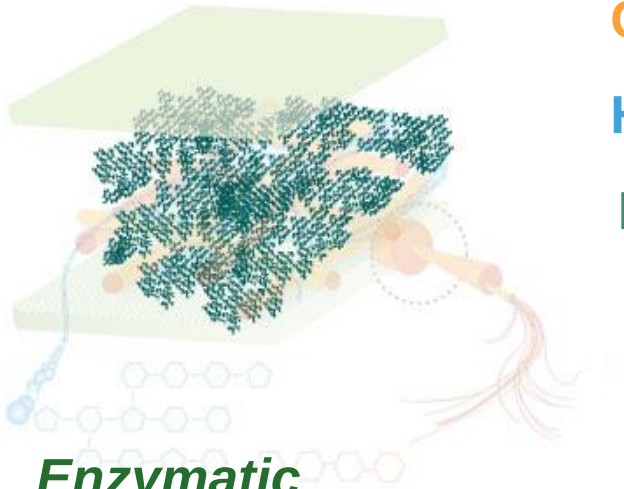
Cellulosic Ethanol Production

Ligocellulosic Biomass



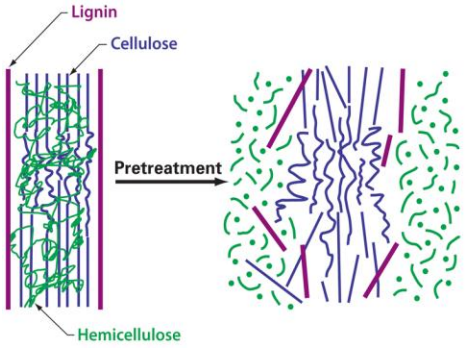


Cellulose

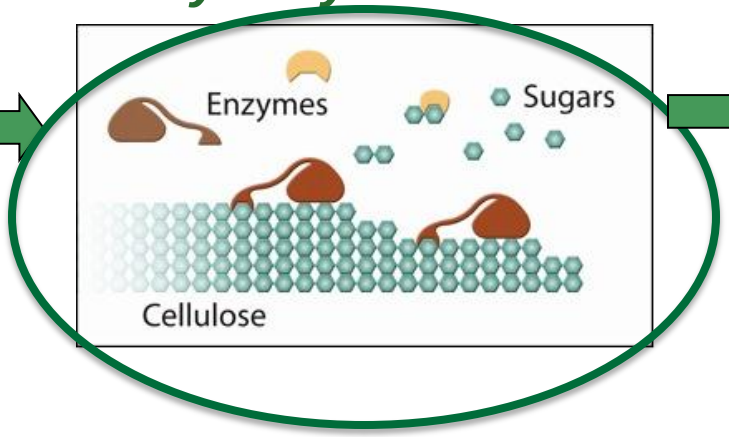
Hemicellulose

Lignin

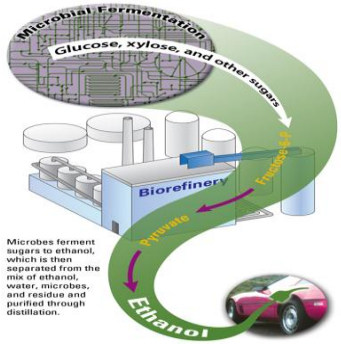
Pre-treatment



Enzymatic Hydrolysis

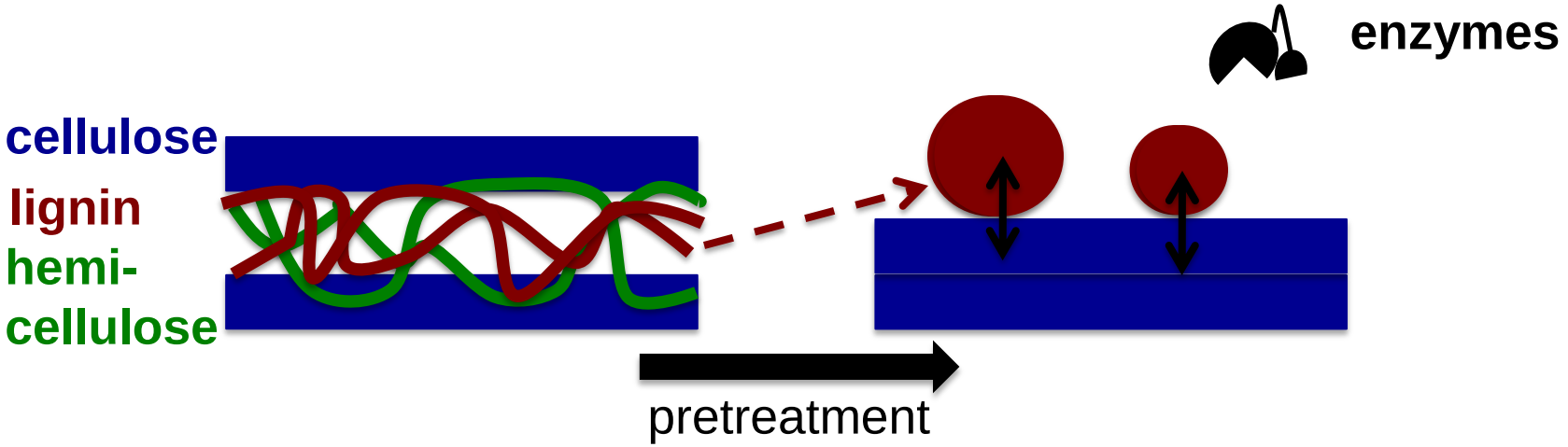


Fermentation



bottleneck: biomass recalcitrance

Physical Origins of Recalcitrance

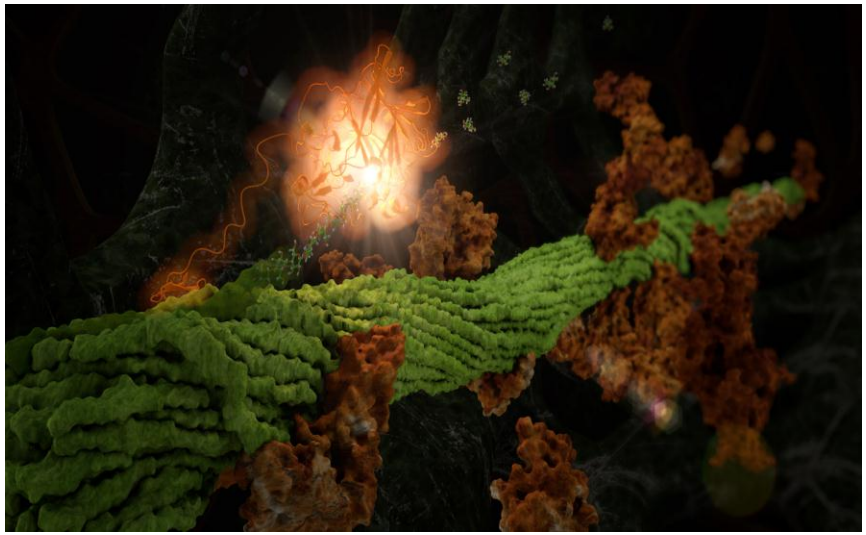


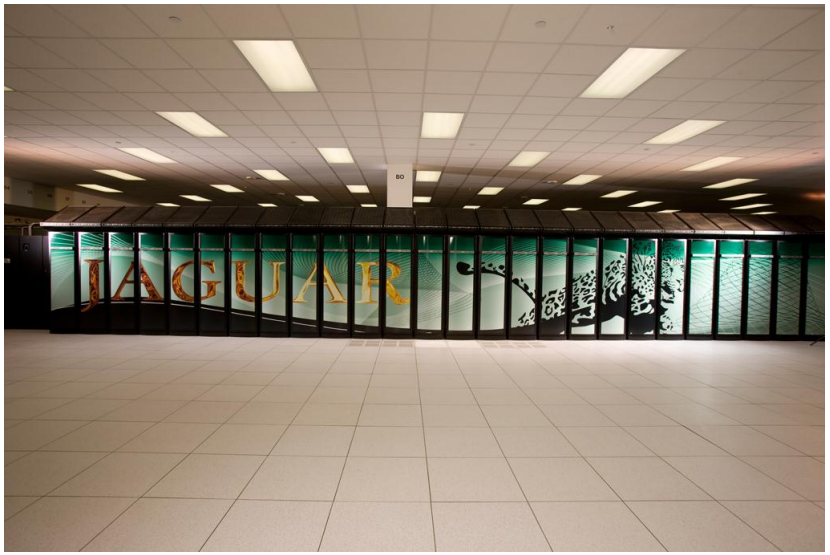
Collapse of lignin

Enzyme:lignin interaction (Structure of lignin aggregates)

Lignin:cellulose association

Petascale Molecular Dynamics Simulation

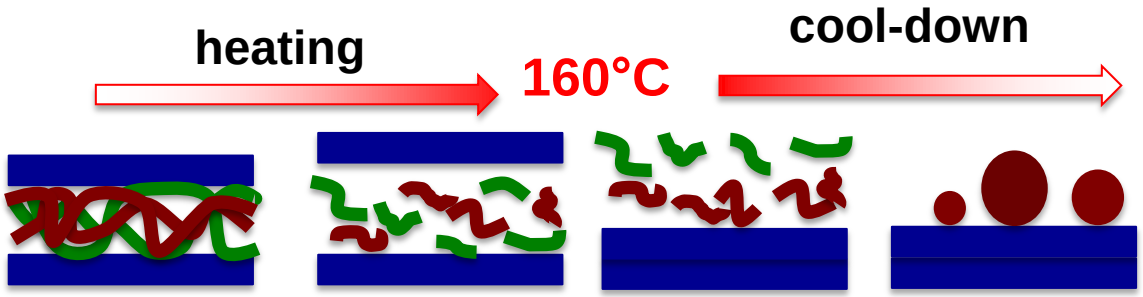




Comparison to Experiments

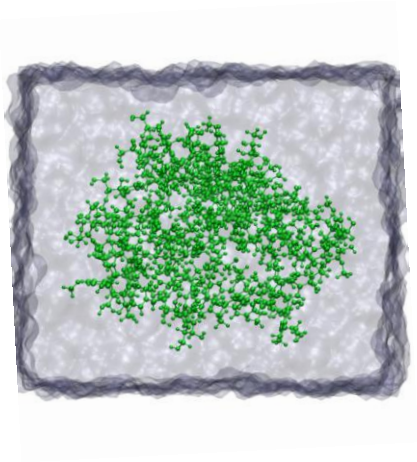
Physical Insights

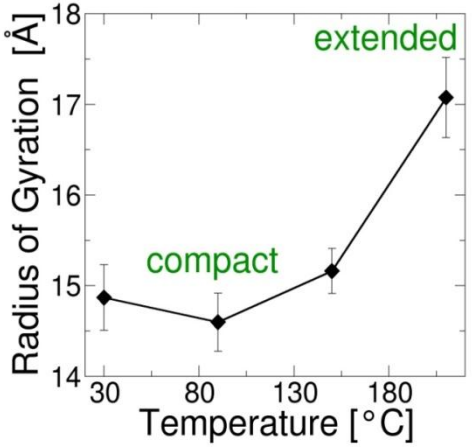
Temperature Dependence of Lignin

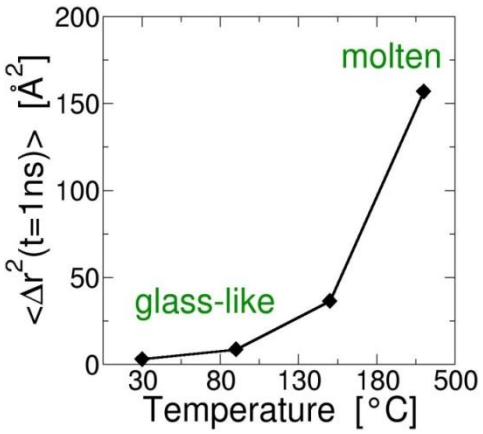


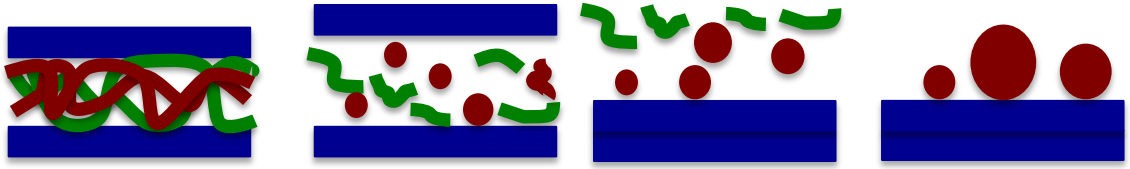
Old: lignin aggregation during cool-down

DOE INCITE







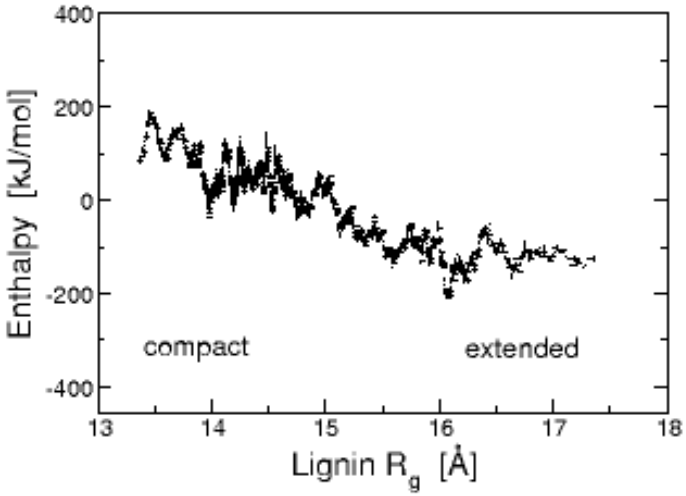


New: lignin aggregation during heating

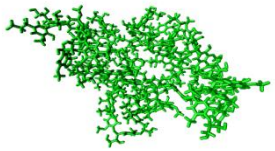
Petridis et al JACS 133 20277 (2011)

Why Does Lignin Collapse at Room Temp?

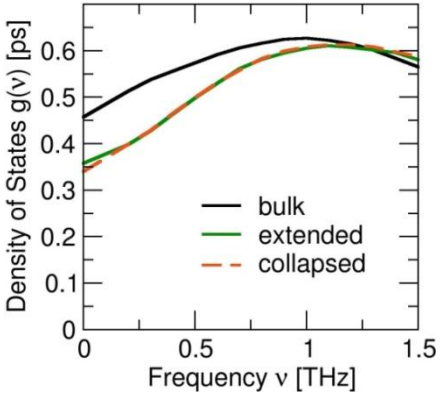
- **Enthalpy**
- ΔH ≈ +200 kJ/mol **Unfavorable**

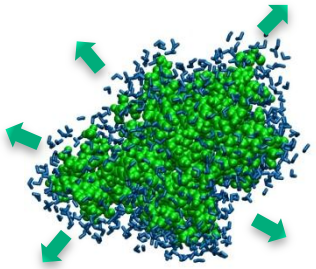


- **Lignin configurational entropy**
- $-T\Delta S_{conf} \approx$ +10 kJ/mol **Unfavorable**



- Hydration **water translational & rotational entropy**
- $-T\Delta S_{t+r} \approx$ -100 kJ/mol **Favorable**



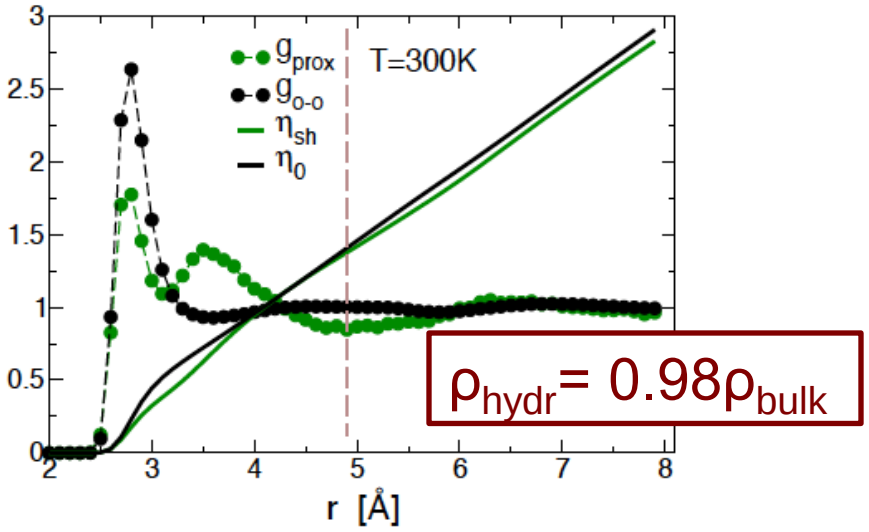


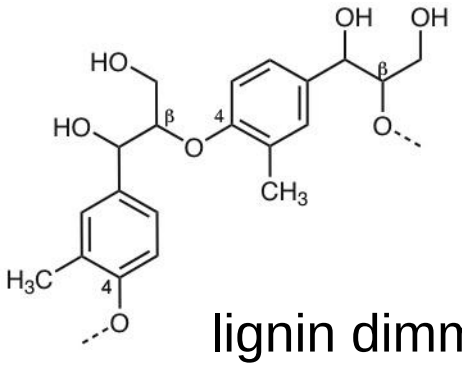
- Hydration **water compressibility**
- $-T\Delta S_{fluc} \approx$ -300 kJ/mol **Favorable**

Collapse Driven by Removal of Entropically Unfavorable Water Molecules from Lignin Surface to Bulk

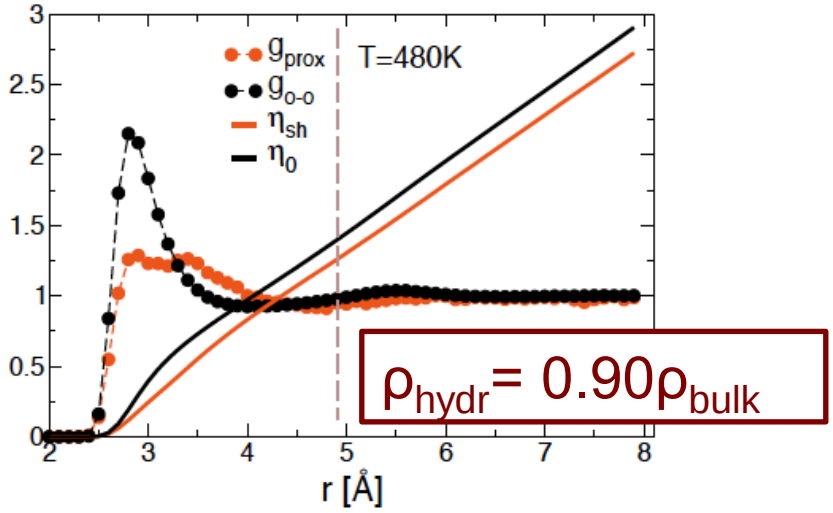
Petridis et al JACS 133 20277 (2011)

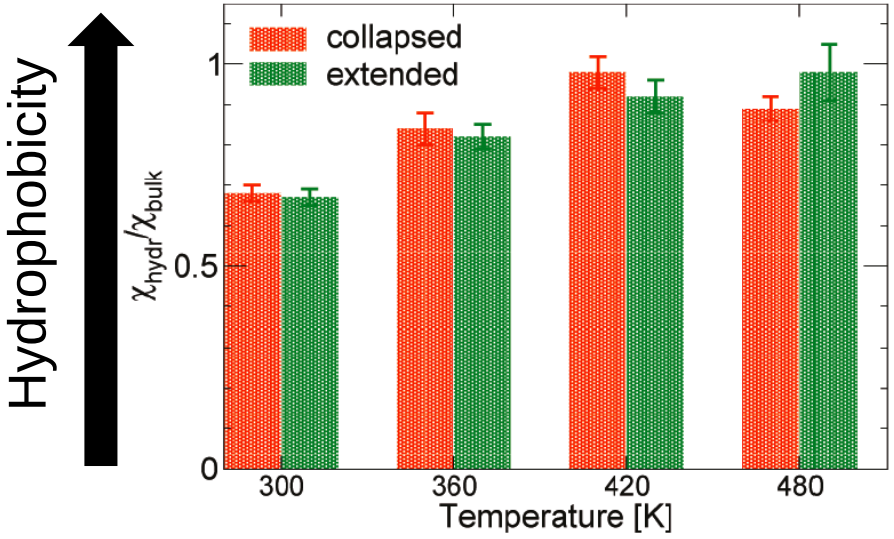
Lignin surface is "wet" at room T, more hydrophobic at high T



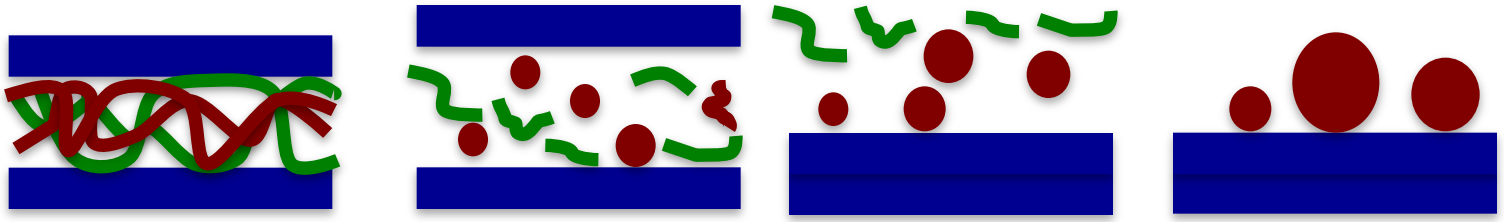


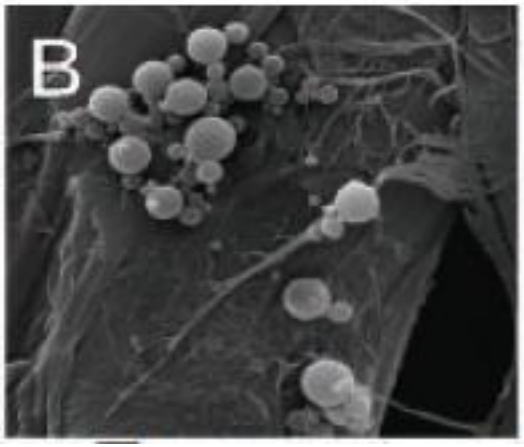
lignin dimmer

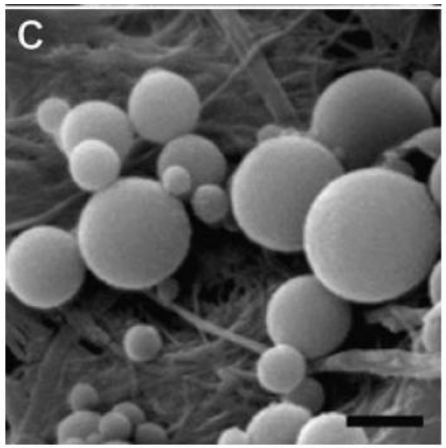


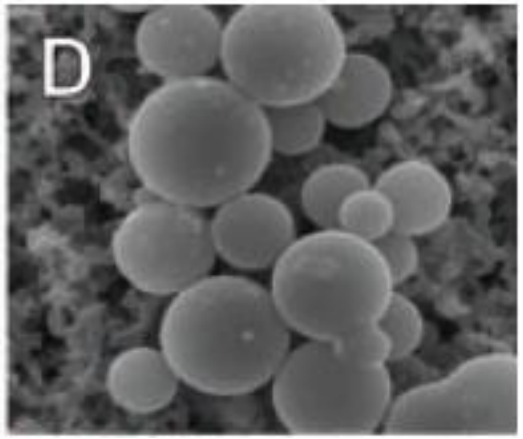


Biomass Pretreatment





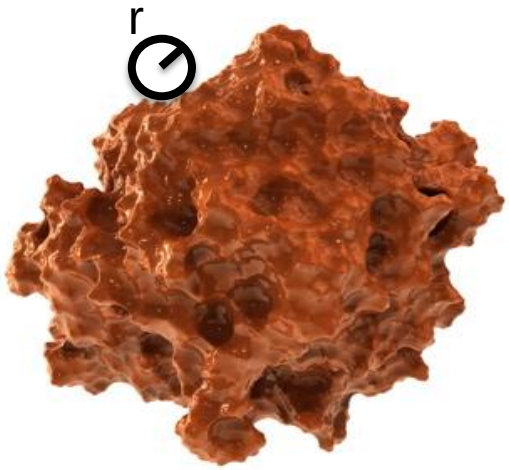




Are Lignin Aggregates Spheres?

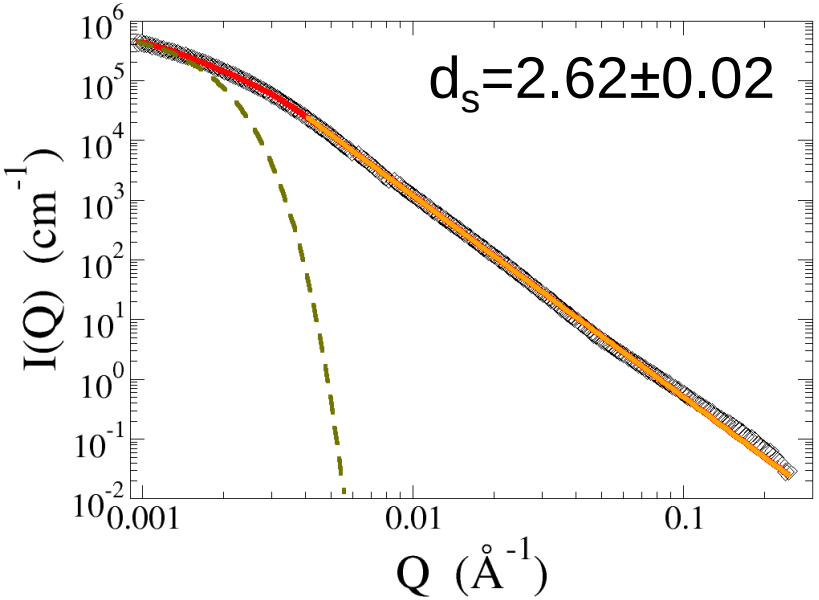
Small-Angle Neutron Scattering

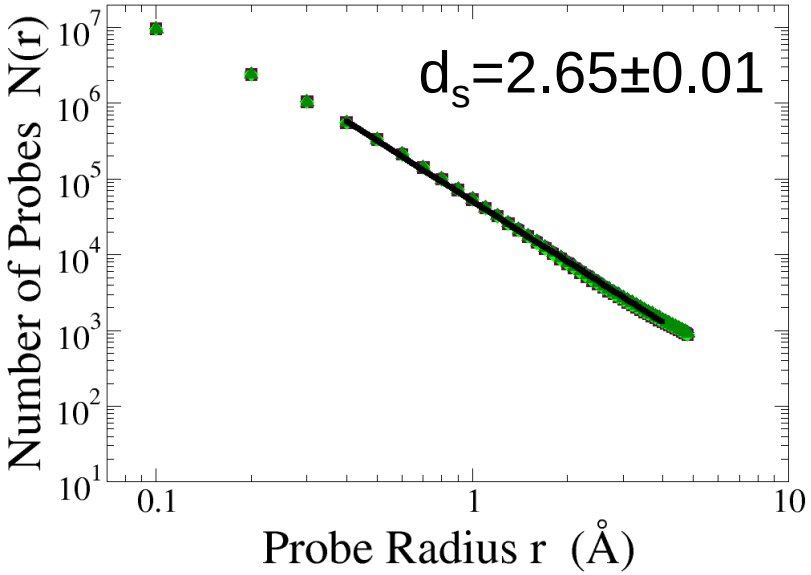
$$I(Q) \propto Q^{d_s - 6}$$



Molecular Dynamics Simulation

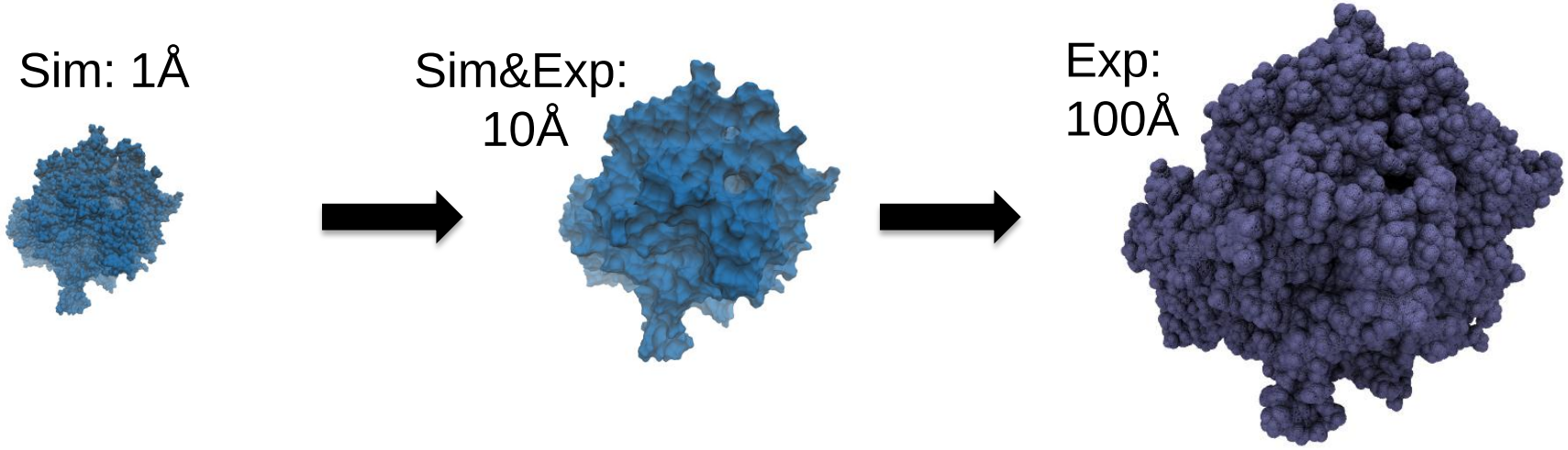
$$N(r) = r^{-d_s}$$



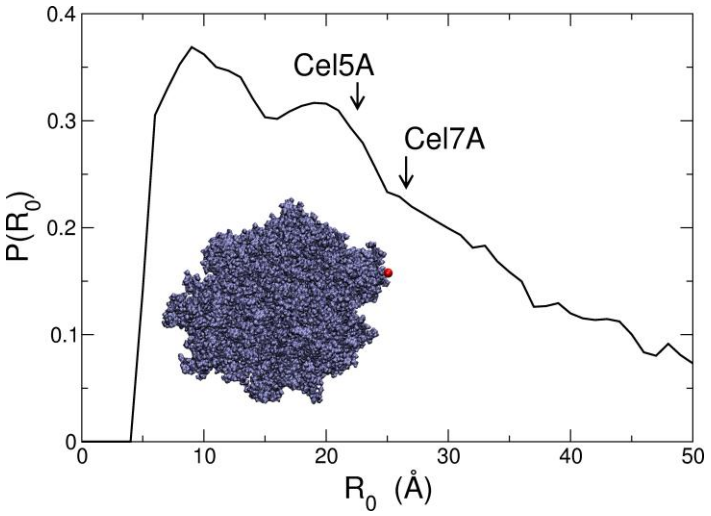


Petridis et al., Phys. Rev. E 83 061911 (2011)

Shape of Surface Invariant Under Change of Scale



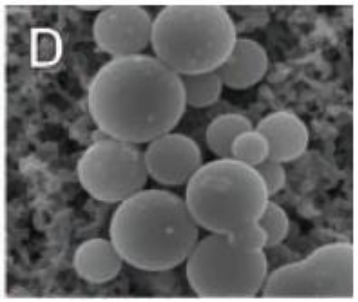
Surface Morphology Impacts Enzyme Inhibition

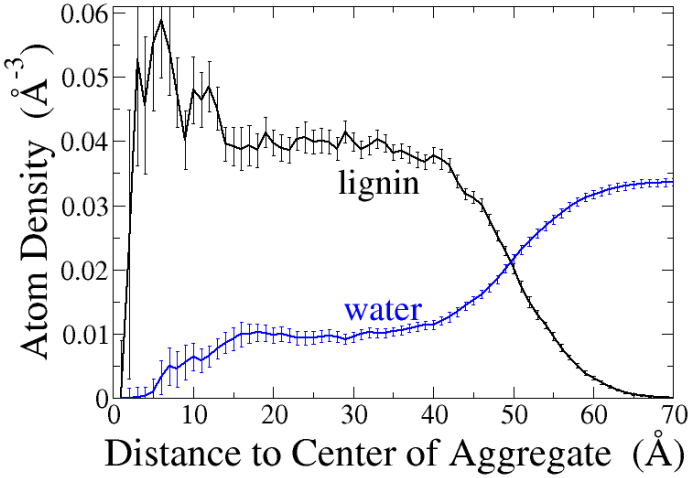


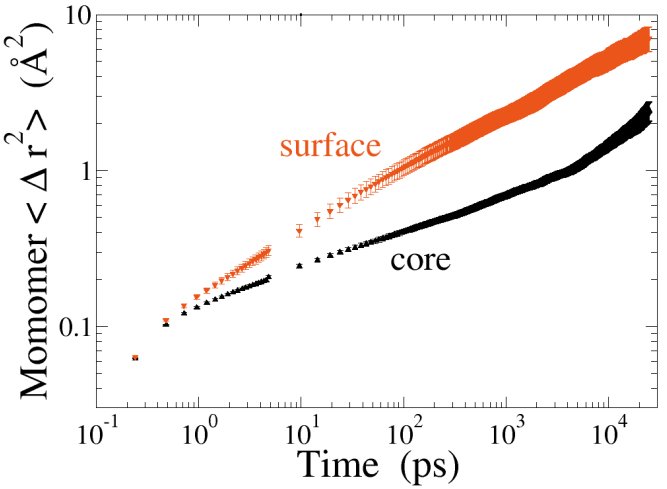
Enzyme:lignin interaction distribution

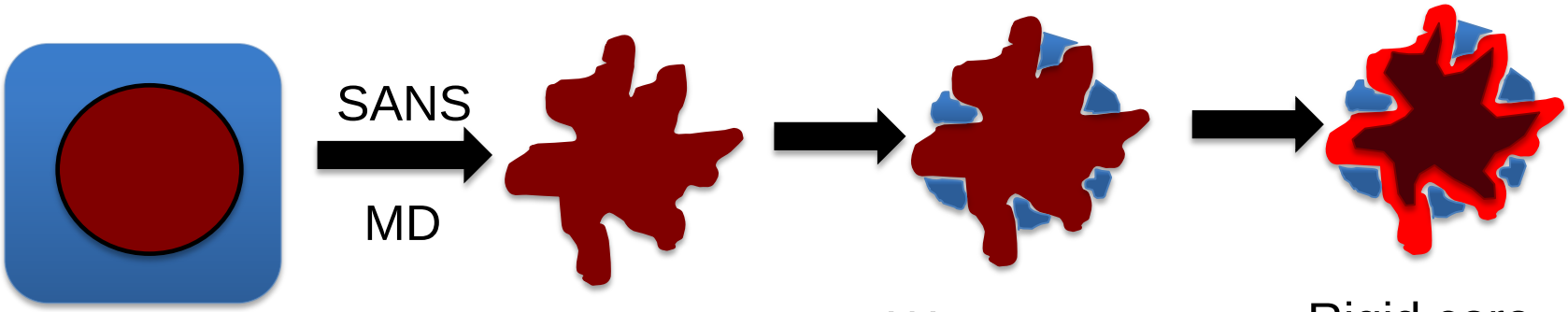
Petridis et al., Phys. Rev. E 83 061911 (2011)

Are Lignin Aggregates Solid Spheres?









rigid sphere

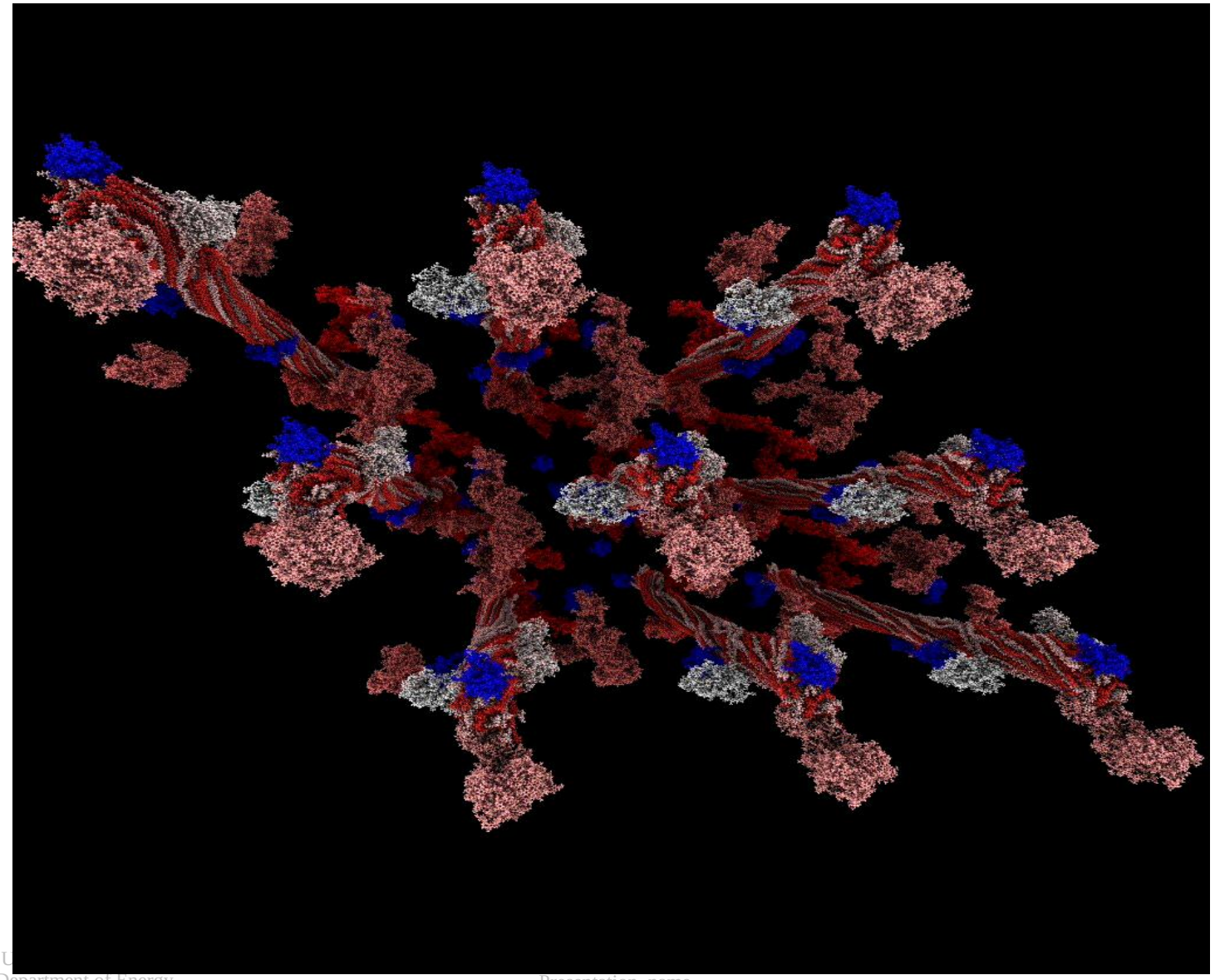
Highly folded surface

Water penetration

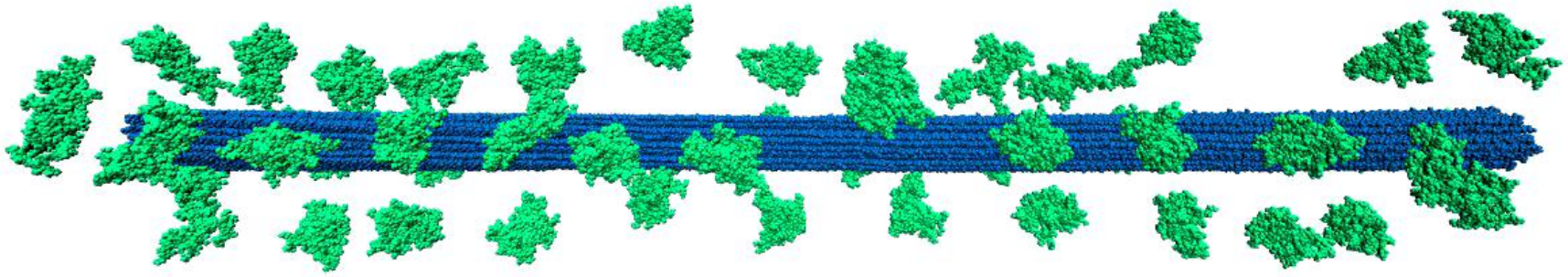
Rigid core
Fluid surface

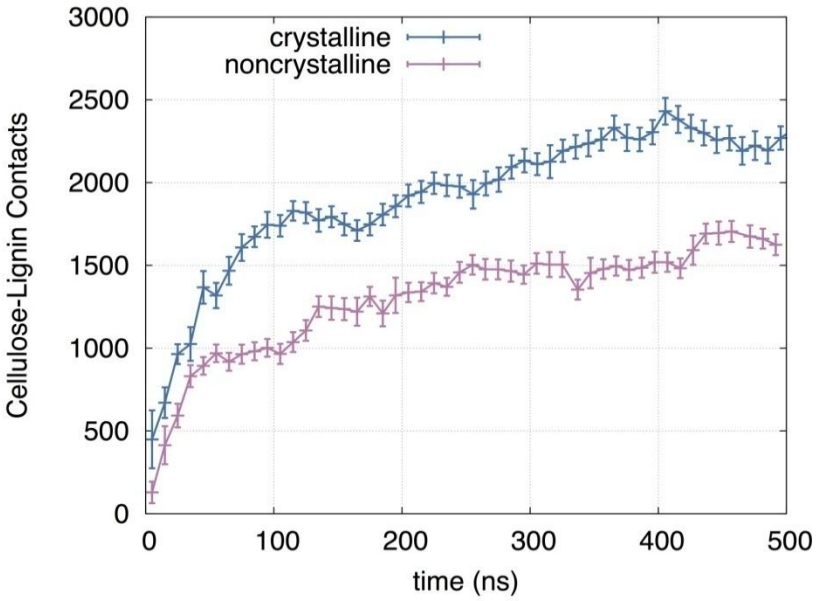
Petridis et al., Phys. Rev. E 83 061911 (2011)

DOE INCITE: Lignocellulose Simulation (30M cpu hours)



Lignin Aggregation & Precipitation on Cellulose

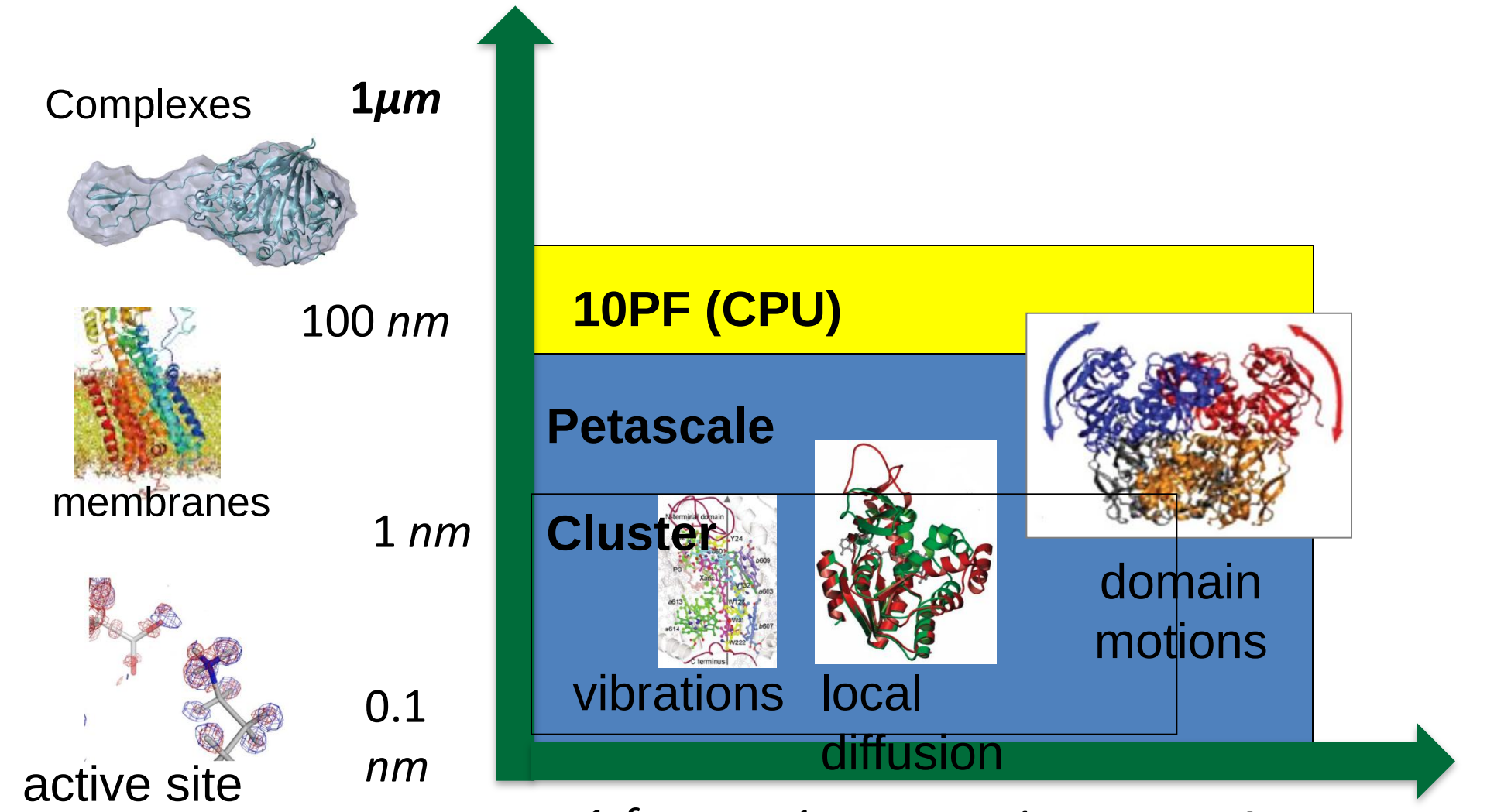




Interface	Interaction Energy Density (kJ/mol/nm^2)
lignin: crystalline cellulose	-49±2
lignin: non-crystalline cellulose	-50±2
water : crystalline cellulose	-94±2
water : non-crystalline cellulose	-107±2

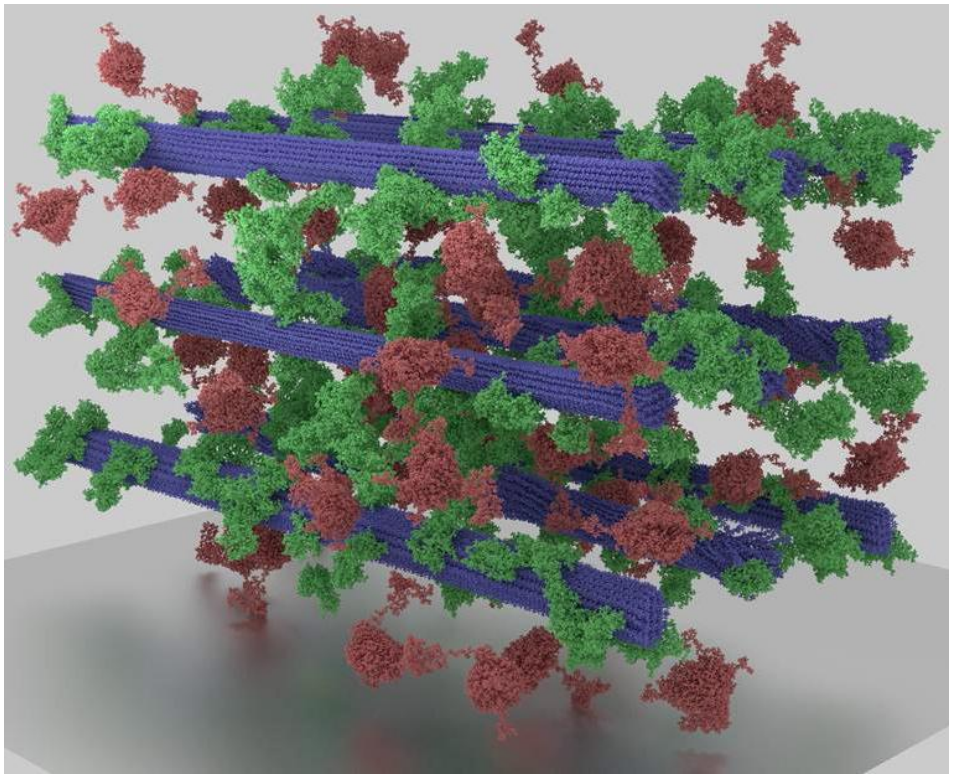
Solvent-Driven Preferential Association of Lignin with Crystalline Cellulose

Multiscale Structure and Dynamics

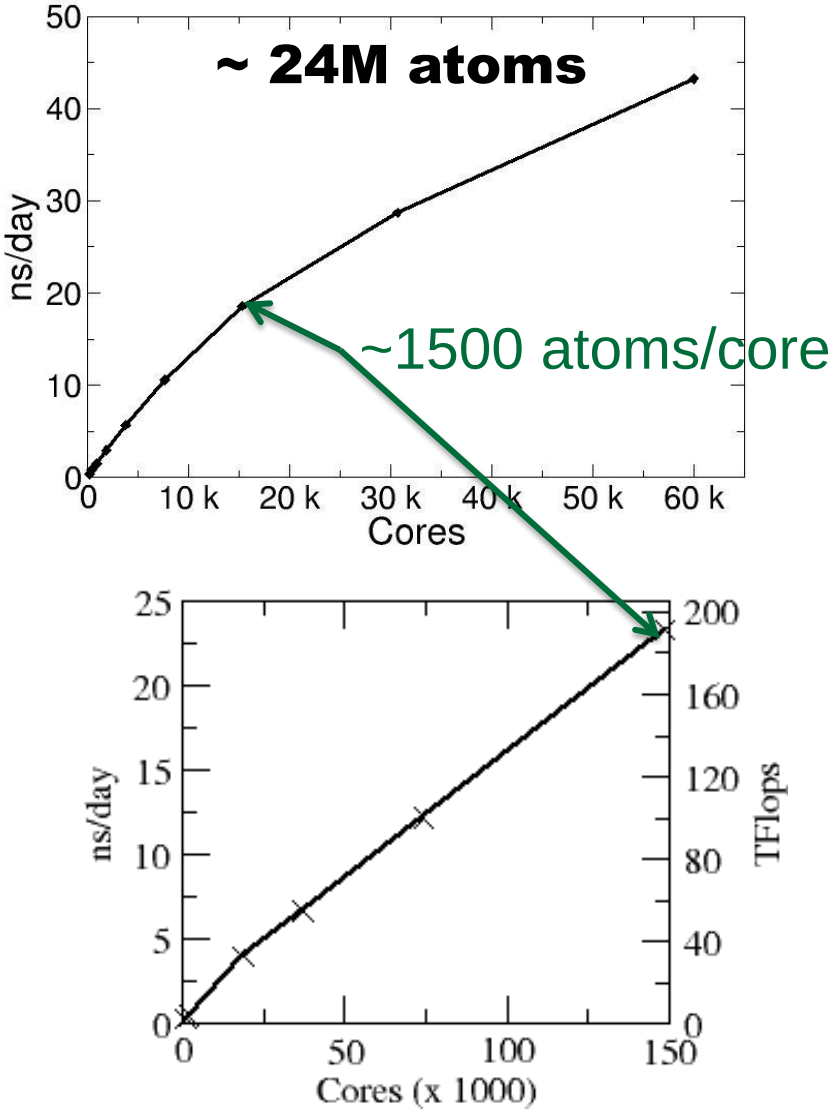


CPU Strong Scaling

Roland Schulz



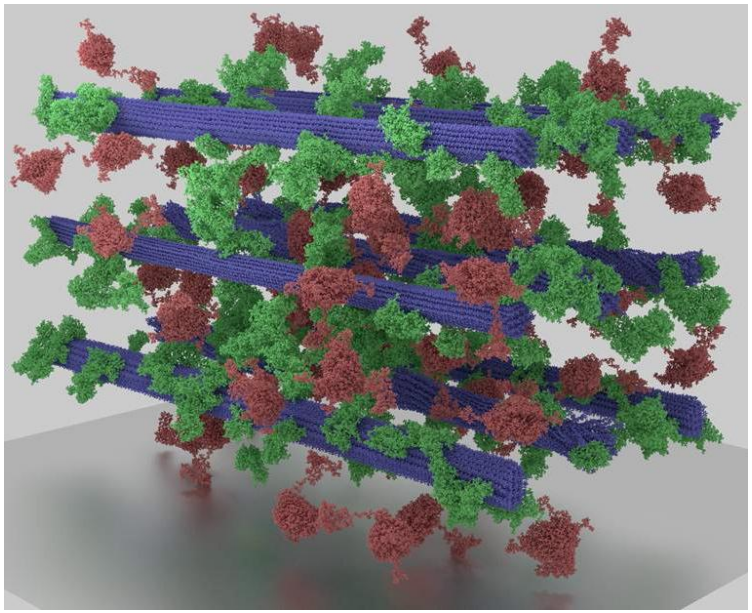
24M-atom capability-class simulation of enzyme binding to pretreated lignocellulose

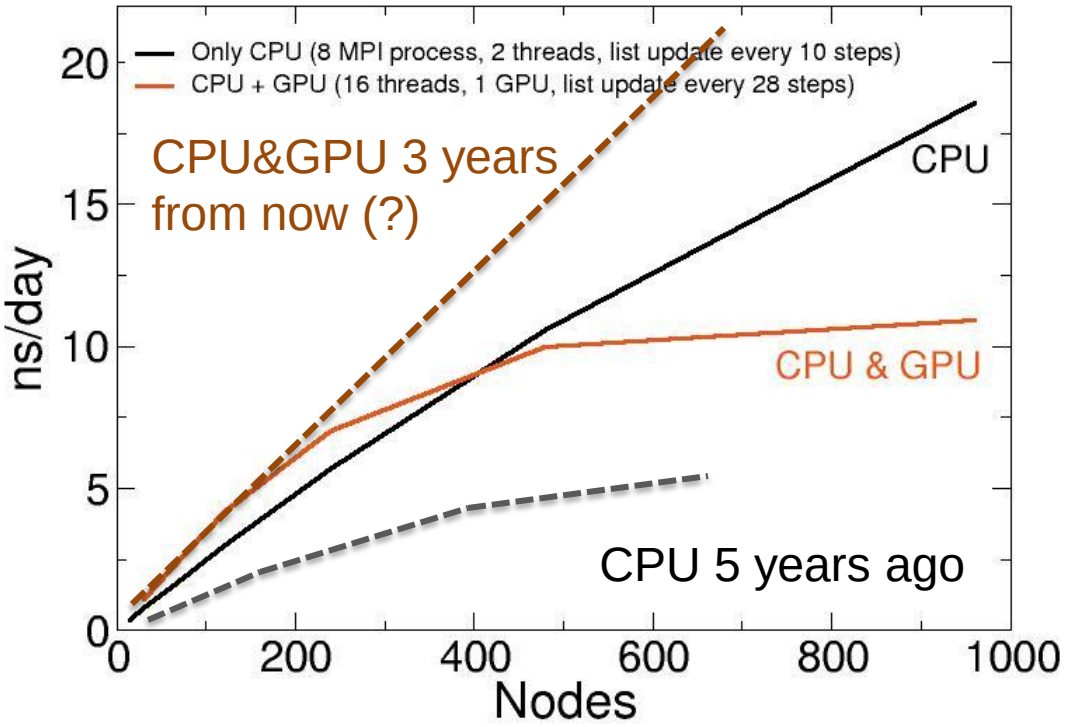


~ 100M atoms

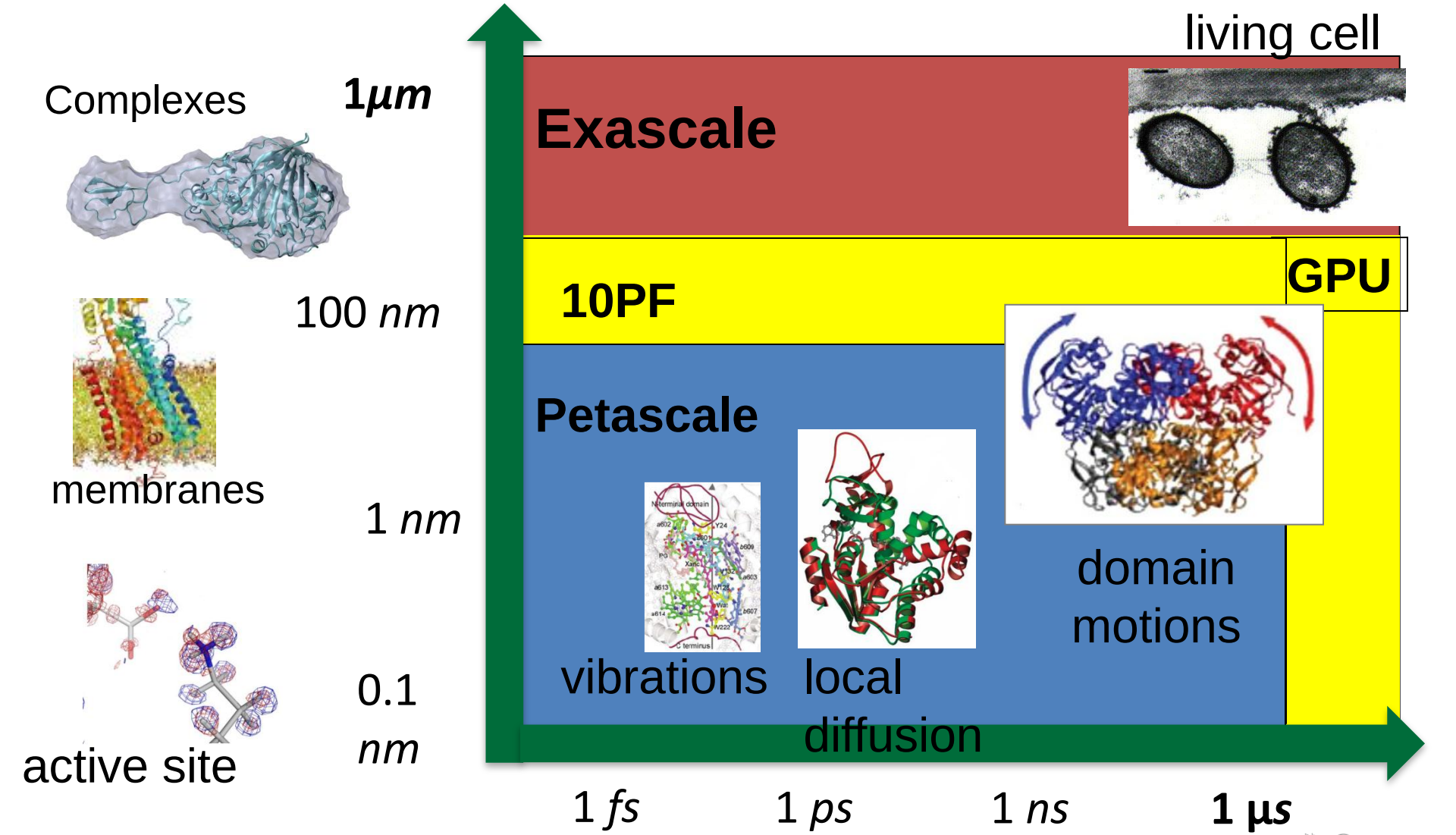
GPU Scaling

Roland Schulz
Szilard Pall
Berk Hess



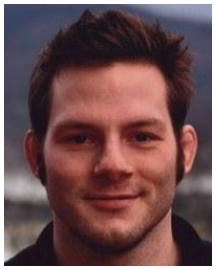


Outlook


Complexes
1μm
100 nm
membranes
1 nm
active site
0.1 nm
living cell
Exascale
10PF
GPU
Petascale
vibrations
local diffusion
domain motions
1 fs
1 ps
1 ns
1 μs

Acknowledgements

Roland Schulz



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OAK RIDGE NATIONAL LABORATORY

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