Multiscale Modeling of Nanostructured Cellulose

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24 June, 2009

2009 International Conference on Nanotechnology for the Forest Products Industry, Edmonton, AB
Outline

- Motivation
- Nanocrystalline cellulose (NCC)
- Ongoing and potential applications of NCC
- Multiscale modeling methods for NCC
- Methodology development at the Theory and Modeling Group, NINT
- Work in progress on NCC
- Conclusions and plans
- Acknowledgement

Motivation

- **Forest products:**
  - Micro- and nanocrystalline cellulose
  - Design of biocompatible functional materials
  - Development of high-value advanced products

- **Nanocrystalline cellulose:**
  - Smallest possible level of structure control
  - Reduced defect occurrence
  - Easy to functionalize
  - Hydrophilicity
  - Acid site distribution

- **Multiscale modeling:**
  - Acid-base properties
  - Self-assembly
  - Solvation
  - Nematics

**Main challenges:**
- Modeling of structures at multiple scales
- Solvation in complex media

**Our methods:**
- Electronic structure
- 3D-RISM + DFT
- 3D-RISM + MD
- Coarse-graining


Water distribution around Iα NCC rod from 3D-RISM
(O (red), H (sea green))
Nanocrystalline cellulose (NCC)

Applications, advantages, and challenges

• Membranes:
  – Fuel cells
  – Kidney dialysis and reverse osmosis
  – Protein separation

• Tissue engineering:
  – Heart valves
  – Bone replacement materials
  – Skin grafts

• Paper:
  – Bio-active
  – Conductive
  – Magnetic

• Liquid crystals, emulsions, and foams

Advantages of NCC:
  – Biocompatible and biodegradable
  – Exceptional mechanical properties
  – Straightforward chemical modification
  – Self-assembly and nematic properties

Challenges to broad NCC applications:
  – Dispersion
  – Compatibilization with existing methods
  – Improved understanding of NCC structure-property relationships
  – Rational design of functional materials to capture the advantages of NCC


Theory and Modeling Group at NINT

Applications ↔ Theory

- nanocatalysts
- nanomaterials
- supramolecular architectures
- biomolecules

Modeling on multiple scales

Electronic Structure methods
- Quantum Chemistry
  - Ab initio HF
  - Ab initio KS-DFT
  - Semi-empirical

Molecular models
- Molecular simulations
  - Monte Carlo
  - Molecular mechanics
  - Molecular dynamics

Continuum
- Effective medium theories
  - GB, PCM, COSMO
  - Energy and Mass Transport Models

Statistical Physics- Integral Equation methods

Gusarov, S.; Kovalenko, A. to be published.
Structure modeling methods for NCC

Electronic structure methods:

• DFT in periodic boundary conditions (PBC):
  – QM treatment of an infinite-length NCC
  – Prediction of reactivity indices for self-assembly
  – COSMO solvation model
  – Polarized atomic charges for solvation modeling

• Quantum mechanics/molecular mechanics (QM/MM):
  – Accurate QM treatment for the reaction site
  – Faster MM method for the rest of the system
  – COSMO solvation model

Multiscale methods:

• 3D-RISM solvation method:
  – Statistical-mechanical treatment of solvent in NVT
  – Accuracy comparable to explicit solvation
  – Provides thermodynamics, solvent distribution, etc.
  – Efficient for slow processes in viscous solvent

• 3D-RISM + DFT (ADF) – QM solute treatment
• 3D-RISM + MD (Amber) – MD solute treatment
• Quantum molecular dynamics (QMD)
• Non-equilibrium statistical mechanics

DFT and QM/MM for prediction of:

• Continuum solvation behavior
• Spectroscopic properties

Stoyanov, S.R.; Gusarov, Kovalenko, A. to be published.
Prediction of aggregation preferences

Intermolecular interactions are determined by:
- van der Walls forces (includes shape matching)
- electrostatic forces (includes H-bonding)
- molecular orbital induced interaction (includes $\pi - \pi$)

We have the capability to predict intermolecular interaction based on the following criteria:

- **Shape matching**
  - good match
  - no match
  - overlap
  - molecules apart

- **Electrostatic matching**

- **Fukui functions matching of Maya asphaltene** (based on the HSAB theory)

- **Global softness**

Advanced methodology for aggregation prediction in large systems based on the Koopmans’ theorem is under development.

Potential Energy Surface (PES) analysis:

- Optimal structure
- Properties - NMR, CD, IR, etc.
- Reactions
- (Nano)catalysis

Implemented in ADF Computational Chemistry package:

- Calculation of solvent-solute forces
- Establish relationships between thermodynamics and hydrophilicity/acid site distribution
- Automatically accounts for buried solvent molecules

Advantages for NCC modeling:

Advantages of 3D-RISM + MD modeling:
• MD of solute in “equilibrated” solvent
• Automatically accounts for buried solvent molecules
• To be released as part of Amber 11 commercial software

Luchko, T.; Gusarov, S.; Kovalenko, A. to be published.
Coarse-grained methods for NCC

Introduce simplifications to atomic scale modeling:

• to remove the faster degrees of freedom
• to treat groups of atoms by single mesoparticles

Electronic structure

\[ V^{\text{meso}}(\vec{r}) = \int f(\vec{r}, r_1, \ldots) V(r_1, \ldots) dr_1 \ldots dr_N \]

Parameters

Experiment

Coarse-graining:

• molecular level
• bead-rod model
• bead-spring model

Prediction of liquid crystal properties

The interfacial properties of anisotropic fluids in the presence of external field can be predicted by using an integral equation approach based on the following coupled set:

1. Ornstein-Zernike equation for spatially inhomogeneous and orientationally anisotropic two-particle correlation function with the Mean Spherical Approximation (MSA) or Kovalenko-Hirata (KH) closures:

\[
h(r_1, r_2, \phi_1, \phi_2) = c(r_1, r_2, \phi_1, \phi_2) + \frac{1}{2\pi} \int_V dr_3 \int_0^{2\pi} d\phi_3 c(r_1, r_3, \phi_1, \phi_3) \rho(r_1, \phi_3) h(r_3, r_2, \phi_3, \phi_2)
\]

2. Lovett-Mou-Buff-Wertheim equations for inhomogeneous and anisotropic one-particle density:

\[
\frac{\partial}{\partial z} \ln \rho(z, \phi) = \frac{1}{k_B T} \frac{\partial}{\partial z} [B(z) \cos \phi] + \int_{-\infty}^{\infty} dz' \int_0^{2\pi} d\phi' \int_0^{\infty} q dq c(q, z, z', \phi, \phi') \frac{\partial \rho(z', \phi')}{\partial z'}
\]

\[
\frac{\partial}{\partial \phi} \ln \rho(z, \phi) = \frac{1}{k_B T} \frac{\partial}{\partial \phi} [B(z) \cos \phi] + \int_{-\infty}^{\infty} dz' \int_0^{2\pi} d\phi' \int_0^{\infty} q dq c(q, z, z', \phi, \phi') \frac{\partial \rho(z', \phi')}{\partial z'}
\]

Modeling of NCC solvation

Work in progress:
• Potential of mean force (PMF)
• Kovalenko-Hirata closure for 3D-RISM – parametrized for systems close to phase transitions
• Statistical distribution of water at 25 and 80°C as well as NaCl (1.0M NaCl aqueous solution)

\[ \text{PMF} = \mu - \mu_S + E_C - E_{C-S} + E_{LJ} - E_{LJ-S} \]

\( \mu = \text{excess chemical potential}, \ E_C = \text{electrostatic energy}, \ E_{LJ} = \text{Lennard-Jones energy}; \ \mu_S, E_{C-S}, \text{and } E_{LJ-S} \text{ are for completely separated NCC rods (distance = 22 Å)} \)

Conclusion and plans

Advantages of modeling:
• Provides a very detailed understanding of structure and properties
• Allows for fast generation and testing of research leads
• Highly cost-effective, as it saves chemicals and equipment

Multiscale modeling yields:
• Prediction of aggregation preferences and hydrogen bonding in solution
• Statistical solvent distribution in molecular and ionic solution at high T
• Solvation thermodynamics, i.e. PMF, ΔH, ΔS, Cp, ΔG, PMV, etc.
• Prediction of liquid crystal behavior
• Correlation of thermodynamics to reactivity

Our plans include the following:
• Investigate NCC thermodynamics in solution
• Understand the relationship between NCC modifications and solubility (hydrophilic-hydrophobic properties)
• Rationally design modified NCC
• Develop advanced functional materials based on NCC
Acknowledgement

Funding sources:
- NINT
- NRC-CNRC
- University of Alberta

Computational resources:
- WestGrid
- University of Alberta Academic Information and Communication Technologies (AICT)
- Centre for Excellence in Integrated Nanotoools (CEIN)

Collaboration contacts:
- Ted Szabo
  Alberta Forestry Research Institute
- Yaman Boluk
- Robert Jost
- Liyan Zhao
  Alberta Research Council
- Mark McDermott
  University of Alberta
- NINT