Materials Genome Initiative for Soft Matter: Computational Challenges

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Activity 2008-2010

- International comparative study
  - Chaired by Sharon Glotzer
    - Life sciences and medicine
    - Materials
    - Energy and sustainability
- Strategic directions workshop
  - Chaired by Peter Cummings
- One of key precursor studies for MGI

Soft Matter

Wikipedia definition

- “[S]ubfield of condensed matter comprising a variety of physical states that are easily deformed by thermal stresses or thermal fluctuations”

  - Examples: Liquids, colloids, polymers, foams, gels, granular materials, some biomaterials
  - Common feature: Predominant physical behaviors occur at energy scale comparable with $k_B T$
    - Quantum aspects generally unimportant
    - Weak dispersion interactions frequently dominate
  - Can be difficult to predict properties directly from atomic or molecular constituents
    - Soft matter often self-organizes into mesoscopic physical structures that are much larger than microscopic scale yet much smaller than the macroscopic scale
      - Macroscopic properties are result of mesoscopic structure
  - Contrast with hard materials
    - Energy scales large by comparison to $k_B T$
    - Relatively easy to predict properties since atoms/molecules are typically in crystalline lattice with no mesoscopic structuring
Characteristics of soft matter make MGI-like screening very difficult

- To accomplish
  
  - computationally, we typically have to perform multiple steps, depending on nature of system
    
    - Simplest case: relatively simple liquid with no mesoscopic structure
      
      - From chemistry, gather or derive forcefields
      - Initialize simulation (molecular dynamics or Monte Carlo, as appropriate)
      - Equilibrate simulation
      - Perform production runs of simulations
      - Statistically average to obtain properties
Room-temperature ionic liquids

- Ionic liquids (i.e., molten salts) made of organic ions whose ability to crystallize is frustrated by organic groups
- Relevant in multiple energy technologies
  - Energy-efficient separations, carbon capture, energy storage as electrolytes for supercapacitors

Ionic Liquids: Designer Solvents for a Cleaner World, James F. Wishart, President’s FY 2005 Budget Request to Congress

\[ \text{C}_4\text{mpip}^+ \]

\[ \text{Tf}_2\text{N}^- \]
Case in Point: RTILs

- RTILs
  - ~9 billion possible RTILs
  - Structured on nanoscale but not mesoscale (based on SAXS and SANS)
    - Atomistic description is appropriate and sufficient
  - Perfect candidates for screening?
    - E.g., for solubility of carbon dioxide
  - Problems:
    - Only ~100 forcefields available for RTILs
    - Hence, to implement MGI-like screening of RTILs needs automated forcefield development capability

- Contrast with screening of metal-organic frameworks
  - 137,953 hypothetical MOF structures generated
  - Each MOF evaluated for methane storage at 35 bar and 298 K using grand canonical Monte Carlo
  - ~300 MOFs had higher methane-storage capacity at 35 bar than current world record

Self Assembly in Soft Matter

- Both RTILs and MOFs share simplifying feature that atomistic description is appropriate
  - *No mesoscopic ordering in RTIL, crystalline (macroscopic) structure for MOFs*

- What about soft matter systems that self-assemble into mesoscopic structures that determine macroscopic properties?
  - **Examples**
    - Amphiphilic molecules/polymers
    - Lipids that assemble into bilayers
  - **Technical challenges**
    - Time to self-assemble
    - Scale of mesoscopic structures
  - **Usual approach**
    - Coarse-graining
      - Systematic, ad hoc, models that exist only at the coarse-grained level
Coarse-Graining

Superposition of fully atomistic and coarse-grained models of n-dodecane. A 3:1 mapping is used, where each CG bead represents 3 CH₂ groups or 2 CH₂ groups and a CH₃ group.

Mapping of fully atomistic model of skin lipid to CG model. Courtesy of Clare McCabe.

Real experimental observations - Often thermodynamic/macroscopic

"Top-down"

Coarse-grained Model

"Knowledge-based"

Classical, empirical Atomistic Model

"Bottom-up"

Real material - “Fundamental” description

E.g., protein folding

Self-Assembling Soft Matter

- **Goal**
  - Chemistry and conditions → Properties

- **For simple case...**
  - E.g., ionic liquids

  - **Chemistry** → **gather**
    - derive
  
  - **Properties**
    - Statistical averaging
    - Production runs
    - Equilibrate atomistic simulation
Self-Assembling Soft Matter

Goal

For simple case...
- E.g., ionic liquids

Chemistry and conditions

Properties

Chemistry

Atomistic forcefield(s)

Initialize atomistic simulation

Production runs

Statistical averaging

Equilibrate atomistic simulation

gather

derive
Self-Assembling Soft Matter

- Bottom-up coarse-grained properties estimation

1. Chemistry
   - gather
   - derive

2. Atomistic forcefield(s)
3. Initialize atomistic simulation
4. Equilibrate atomistic simulation
5. Production runs
6. Statistical averaging

7. CG forcefield
8. CG production runs
9. Statistical averaging
10. Inversion to atomistic

Properties
Self-Assembling Soft Matter

- Bottom-up coarse-grained properties estimation

1. Chemistry
   - Gather
   - Derive

2. Atomistic forcefield(s)
   - Initialize atomistic simulation

3. Statistical averaging
   - Production runs
   - Equilibrate atomistic simulation

4. CG forcefield
   - CG production runs
   - Inversion to atomistic

5. Properties
   - Statistical averaging
Self-Assembling Soft Matter

- Bottom-up coarse-grained properties estimation

1. Chemistry
   - gather
   - derive

2. Atomistic forcefield(s)
   - Initialize atomistic simulation

3. Statistical averaging
   - Production runs
   - Equilibrate atomistic simulation
   - GPU computing

4. CG forcefield
   - CG production runs
   - Statistical averaging

5. Properties
   - Inversion to atomistic

Diagram: Flowchart illustrating the process of bottom-up coarse-grained properties estimation in self-assembling soft matter.
Self-Assembling Soft Matter

- **Bottom-up coarse-grained properties estimation**

1. **Chemistry**
2. **Atomistic forcefield(s)**
   - Gather
   - Derive
3. **Initialize atomistic simulation**
4. **Equilibrate atomistic simulation**
5. **Production runs**
6. **Statistical averaging**
7. **Inversion to atomistic CG forcefield**
8. **Statistical averaging**
9. **CG production runs**
10. **Properties**
11. **Inversion to atomistic**
Self-Assembling Soft Matter

Within this component of overall workflow...

- **Specialized methods to accelerate calculations**
  - Monte Carlo methods (e.g., configurational bias)
  - Parallel tempering
  - Rare events techniques
  - ....

- **Specialized methods to accommodate self assembly**
  - Constant stress ensemble
  - ....

- **Specialized property sampling methods**
  - E.g., free energy methods
Self-Assembling Soft Matter

- Bottom-up coarse-grained properties estimation

1. Chemistry
2. Atomistic forcefield(s)
3. Initialize atomistic simulation
4. Production runs
5. Statistical averaging
6. Equilibrate atomistic simulation
7. CG production runs
8. Inversion to atomistic
9. CG forcefield
10. Statistical averaging
11. Properties

Gather
Derive
Multiple methods for obtaining CG forcefield

- **Structure matching**
  - E.g., iterated Boltzmann inversion*

- **Force matching**

Choice of CG method strongly coupled to properties to be calculated

- **CG simulations cannot reproduce all properties of atomistic system**
  - Method should preserve properties of interest

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MGI-like computational screening for soft matter relies on complex scientific workflows

- How to automate?
- One acceleration scenario, assuming transferable CG forcefields

Challenges
Challenges

- Coarse-graining often means running many similar atomistic simulations
  - Data management = reusability

- Hybrid materials....

  Hard materials  Hybrid materials  Soft materials
  Metal-organic frameworks  Polyhedral oligomeric silsesquioxanes

- The three V’s
  - Validation, validation, validation
    - Atomic, molecular and nanoscale experimental probes (especially X-ray and neutron sources at DOE and NIST) provide capabilities for validation of computational approaches, particularly to nanoscale structure and dynamics
Challenges

- Interfaces
  - Critically important in multiple applications
    - Energy storage, catalysis, separation processes,...
    - Combines issues of soft and hard materials, often synergistically
      - *Fluid Interface Reactions Structure and Transport (FIRST) Energy Frontier Research Center*
Understanding Supercapacitors

- Nano-porous electrodes
  - Micropores (<2nm) increase specific surface area
  - Anomalous increase of capacitance is observed experimentally

![Graph showing normalized capacitance vs. pore size for different carbon samples.](image)

- New results for microporous activated carbon and mesoporous activated carbon.
- Traditional view

![Chemical structures of EMI cation and TFSI anion.](image)

- 1.5 M solution of tetraethylammonium tetrafluoroborate in acetonitrile.
Goal is to reconcile conflicting experiments

Simulation setup

- Nanoslits filled with room-temperature ionic liquids (RTILs)
  - Electrolyte: [emim+]\([\text{Tf}_2\text{N}^-]\)
  - Electrode: slit-shaped pore
  - Three layers of graphene sheets
  - Slit width \((d)\): 0.67 ~ 1.8 nm
  - Applied potential: ~ 1.41 V
  - NPT: 333K, 1 atm
MD Simulation

- Simulation setup
Capacitance Dependence on Micropore Size

- Normalized capacitance as a function of slit width (C-d curve)

- $d = 0.7 \sim 1.0$ nm: anomalous increase
- $d < 0.7$ nm: decreases with pore size
- 1$^{st}$ peak agrees will with experiments
- $d > 1.0$ nm: 2$^{nd}$ peak is a new feature