Development of quantitative coarse-grained simulation models for polymers

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Education/Outreach: New Visions, Molecularium™
Motivation

- Polymer blend phase behavior
  - Miscibility/immiscibility of polyolefins

- Self-assembly of block copolymers to form novel micro-structured materials

Applications
Hierarchy of Length and Time Scales

molecular scale

polymer coil

polymer melt/continuum

persistance length \(\sim 10\text{Å}\)

bond length \(\sim 1\text{Å}\)

10\(^{-15}\) to 10\(^{-12}\) sec

\(~ 100\text{Å}\)

10\(^{-8}\) to 10\(^{-4}\) sec

\(> 100\text{Å}\)

\(O(1\text{sec})\)
Coarse-graining

Examples: Lattice models or bead-spring chains, dissipative particle dynamics methods

Basic idea: Integrate over (unimportant) degrees of freedom

How do we coarse-grain atomically detailed systems without a significant loss of chemical information?

Do coarse-grained systems provide correct description of structure, thermodynamics, and dynamics of a given atomic system?
Coarse-graining of Polymer Simulations

Goal: To develop coarse-grained descriptions to access longer length and timescales

How do we derive physically consistent particle-particle interaction potentials?

Basic idea

One CG particle describes $n$ carbons of the detailed polymer
Coarse-graining method

• Perform molecularly detailed simulations of polymers

• Define coarse-grained beads by grouping backbone monomers

• Calculate structural correlations between coarse-grained beads

• Determine effective bead-bead interactions that reproduce coarse-grained correlations using Inverse Monte Carlo -- uniqueness?
Detailed molecular dynamics simulations

- Classical molecular dynamics

- \( n \)-alkanes - C16 to C96
  
  (M. Mondello et al. JCP 1998)

- 50 to 100 chains

- \( T = 403K \) \( P = 1 \) atm

- time = 5 to 10 ns
structural details are lost with increasing the level (n) of coarse-graining process
Coarse Graining Intramolecular Correlations
Inverse Monte Carlo simulation

choose a trial potential, e.g.,
\( \varphi(r) = 0 \)

run Monte Carlo simulation
with trial potential

\( g(r) = g_{\text{target}}(r) ? \)

update trial potential
\[ \varphi_{\text{new}}(r) = \varphi_{\text{old}}(r) + f \ln \left( \frac{g(r)}{g_{\text{target}}(r)} \right) \]

No

Yes

done
Coarse Grained Potential

\[ E_{\text{total}} = E_{\text{inter}} + E_{\text{intra}} \]

\[ = \sum_{\text{pairs}} \varphi_{\text{inter}}(r) + \sum_{12\text{pairs}} \varphi_{12\text{intra}}(r) \]

\[ + \sum_{13\text{pairs}} \varphi_{13\text{intra}}(r) + \sum_{14\text{pairs}} \varphi_{14\text{intra}}(r) + \ldots \]
Inter-bead Interactions

Inter-bead radial distribution function

Effective interaction potential

before IMC

after IMC
Intra-bead Interactions

12-intra-bead “bonded” interactions
\( \varphi_{12}(r) \)

13-intra-bead interactions
\( \varphi_{13}(r) \)

14-intra-bead interactions
\( \varphi_{14}(r) \)

Potential \( (kT) \):

- \( \varphi_{12}(r) \):\n  - Graph showing potential vs. distance.
  - Potential increases with distance.

- \( \varphi_{13}(r) \):\n  - Graph showing potential vs. distance.
  - Potential decreases with distance.

- \( \varphi_{14}(r) \):\n  - Graph showing potential vs. distance.
  - Potential has a minimum at a certain distance.
Oligomer conformation distribution

radius of gyration distribution for C96

CG method reproduces conformational statistics of molecular oligomers
Radius of Gyration and Effect of Temperature

\[ R_g = AM_w \]

\[ R_g = KM_w^{1/2} \]

Temperature:
- 403K
- 503K

\[ K_{CG} = 0.45 \quad 0.40 \]

\[ K_{expt} = 0.45 \quad 0.42 \]

excellent agreement with experiment
Polymer Conformation Distribution

radius of gyration distribution (403K)

\[ R_g^* = \frac{R_g}{\langle R_g^2 \rangle^{1/2}} \]

polymer conformational space efficiently explored
Conclusions

• CG method maps molecular scale correlations to coarse-grained potentials

• Coarse grained potential simpler than molecular potential and can be extended to polymer simulations while preserving molecular identity

• Not limited to polymeric species (e.g., buckyballs/nanocomposites)

• Path Forward
  - Polyolefin blends
  - Block copolymer assembly
  - Dynamics?
Hydra: H atom

Water molecule

Biological world

Mr. Carbone
Thank you!