Development of quantitative coarse-grained simulation models for polymers

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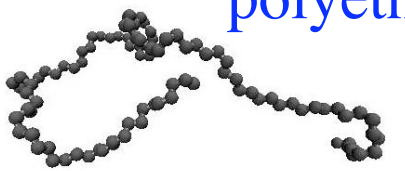
Education/Outreach: New Visions, Molecularium™

Motivation

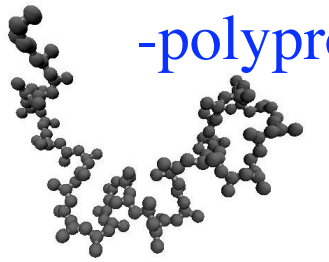
Applications

- Polymer blend phase behavior
  - Miscibility/immisciblity of polyolefins

polyethylene

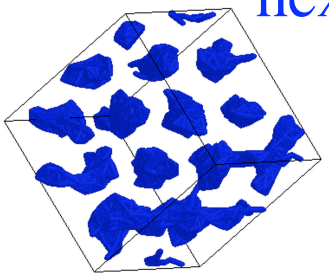


atactic -polypropylene

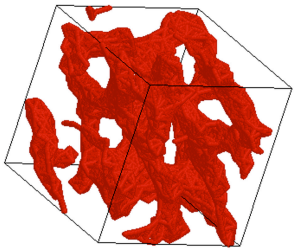


- Self-assembly of block copolymers to form novel micro-structured materials

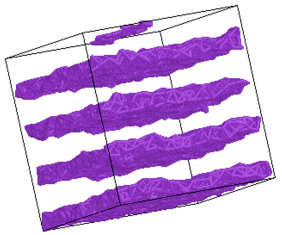
hexagonal



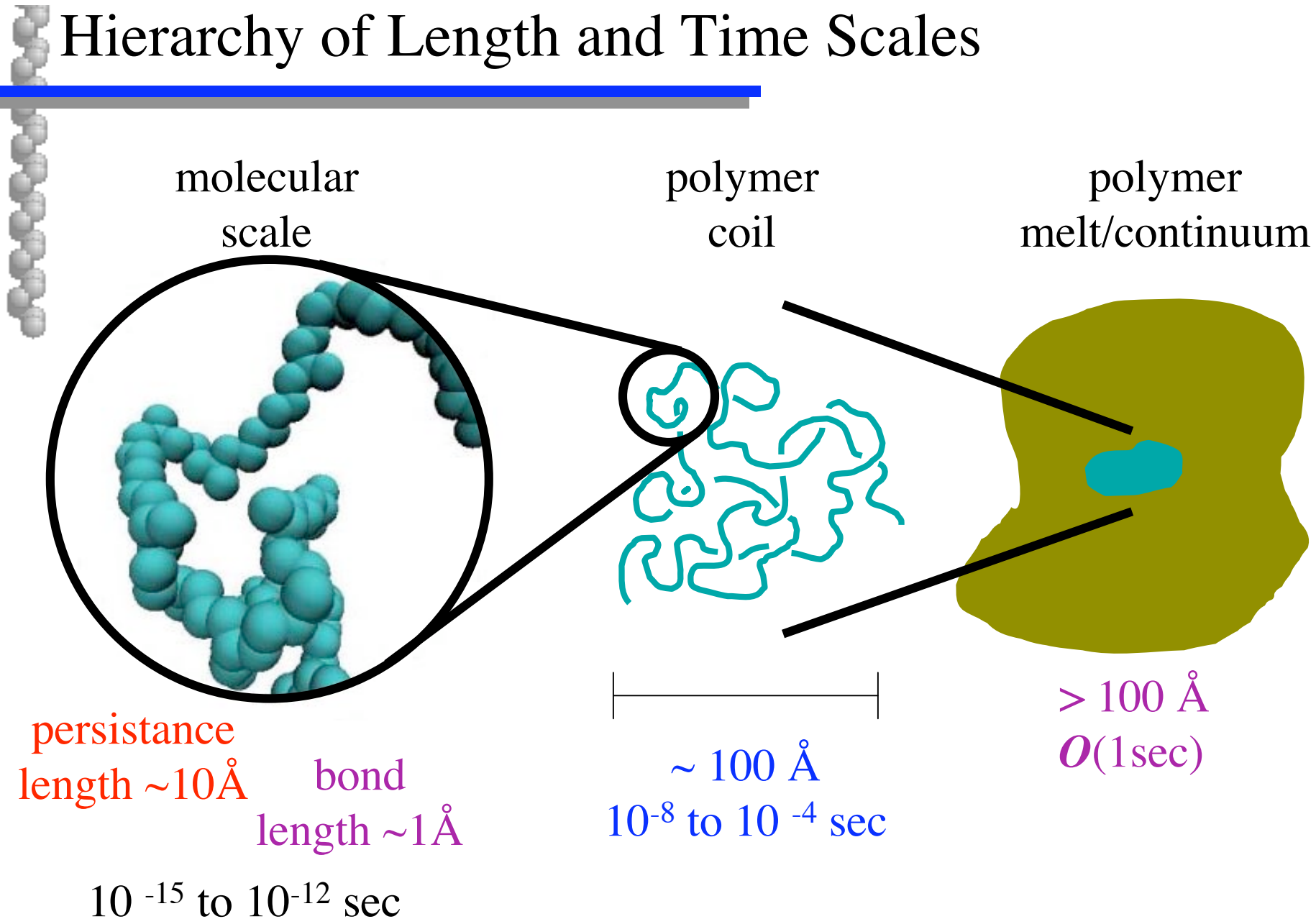
bicontinuous



lamellar



Hierarchy of Length and Time Scales



Coarse-graining

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

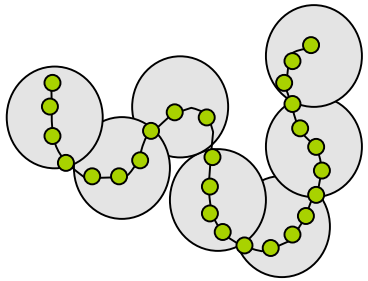
Basic idea: Integrate over (unimportant) degrees of freedom

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

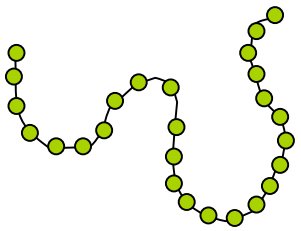
Do coarse-grained systems provide correct description of structure, thermodynamics, and dynamics of a given atomic system?

Coarse-graining of Polymer Simulations

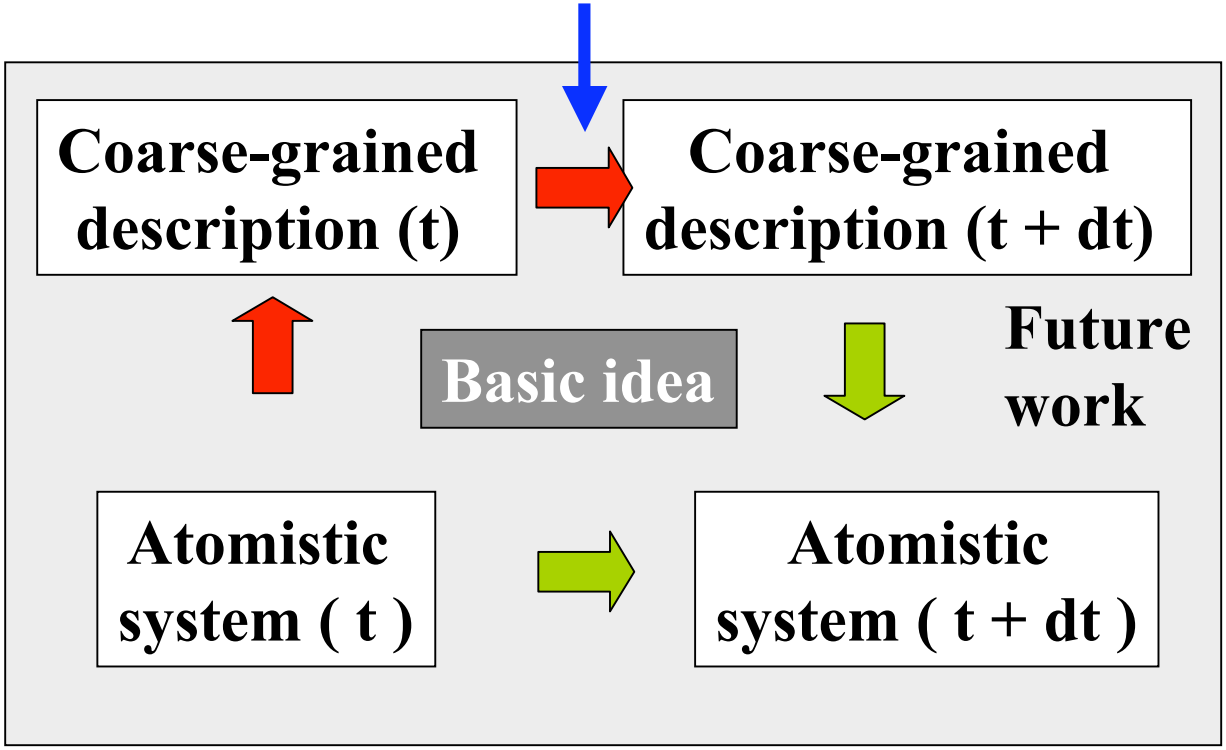
Goal: To develop coarse-grained descriptions to access longer length and timescales



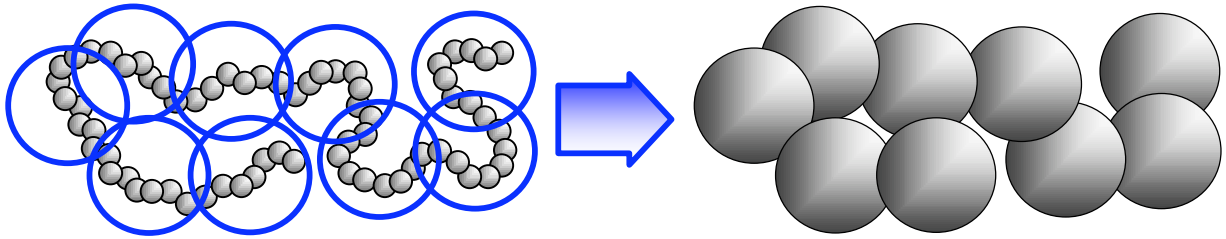
One CG particle describes *n* carbons of the detailed polymer



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



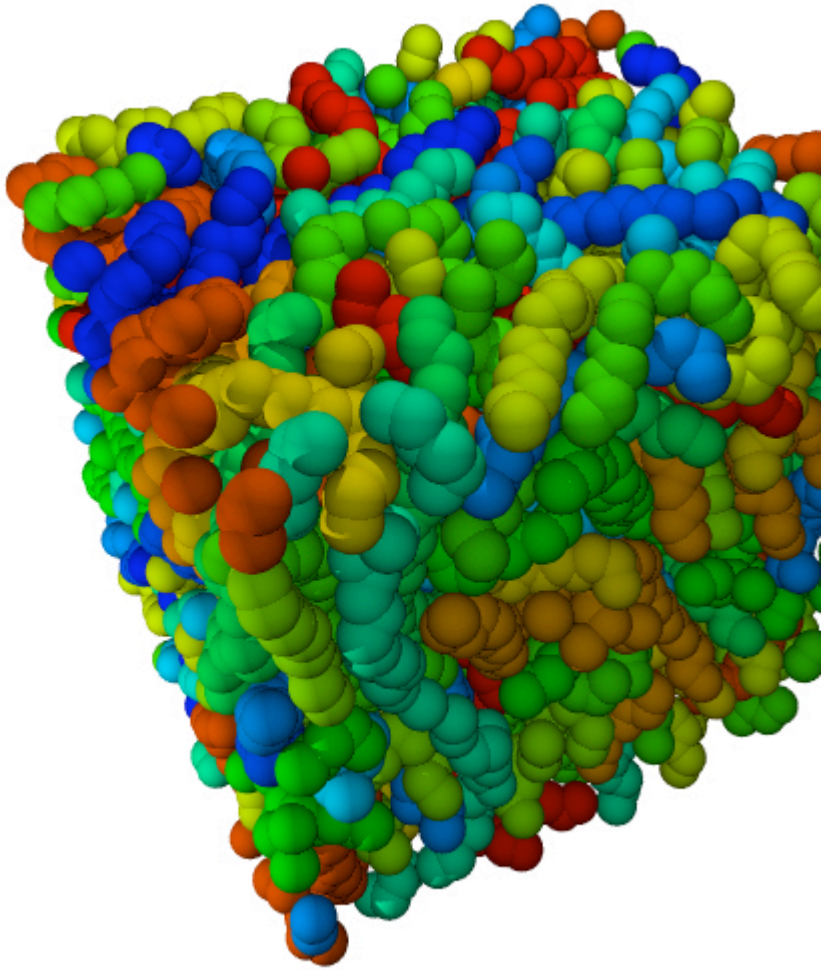
Coarse-graining method



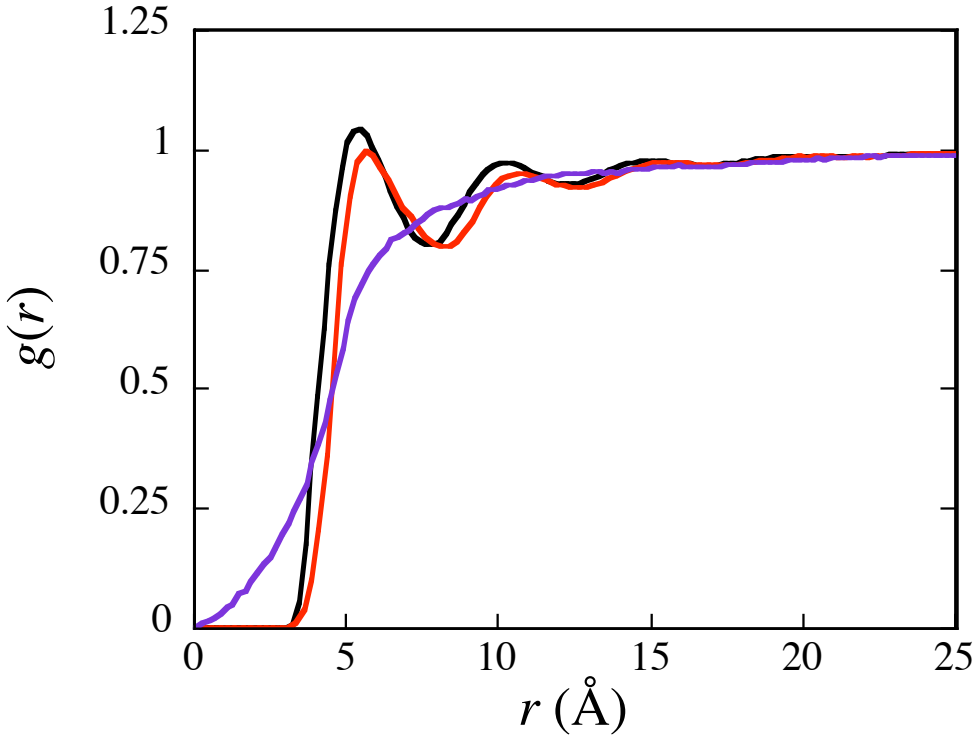
- Perform molecularly detailed simulations of polymers
- Define coarse-grained beads by grouping backbone monomers
- Calculate structural correlations between coarse-grained beads
- Determine effective bead-bead interactions that reproduce coarse-grained correlations using Inverse Monte Carlo
  -- uniqueness?

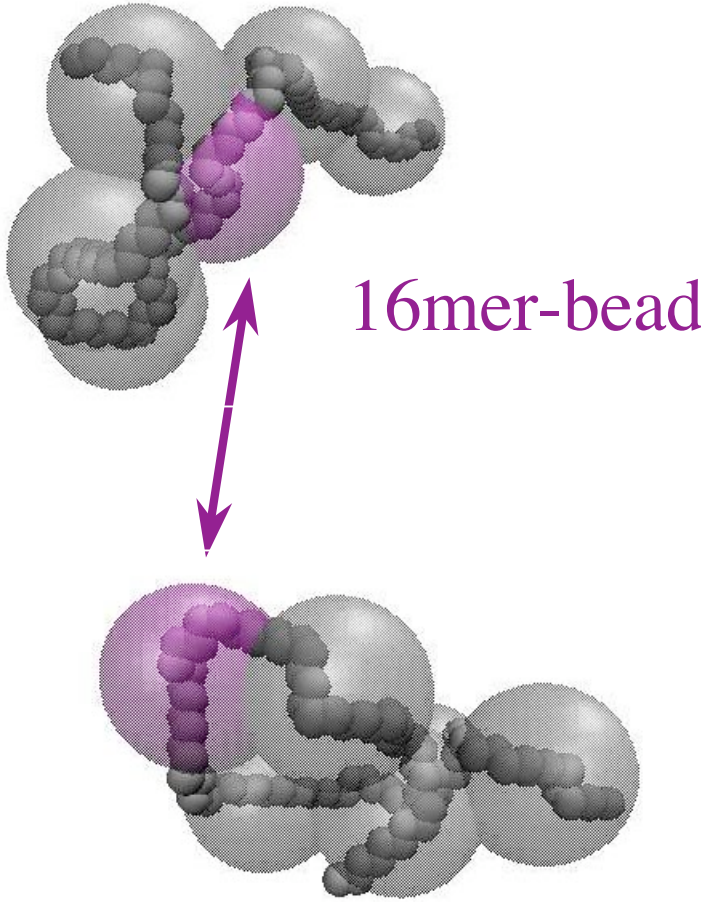
Detailed molecular dynamics simulations

- 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



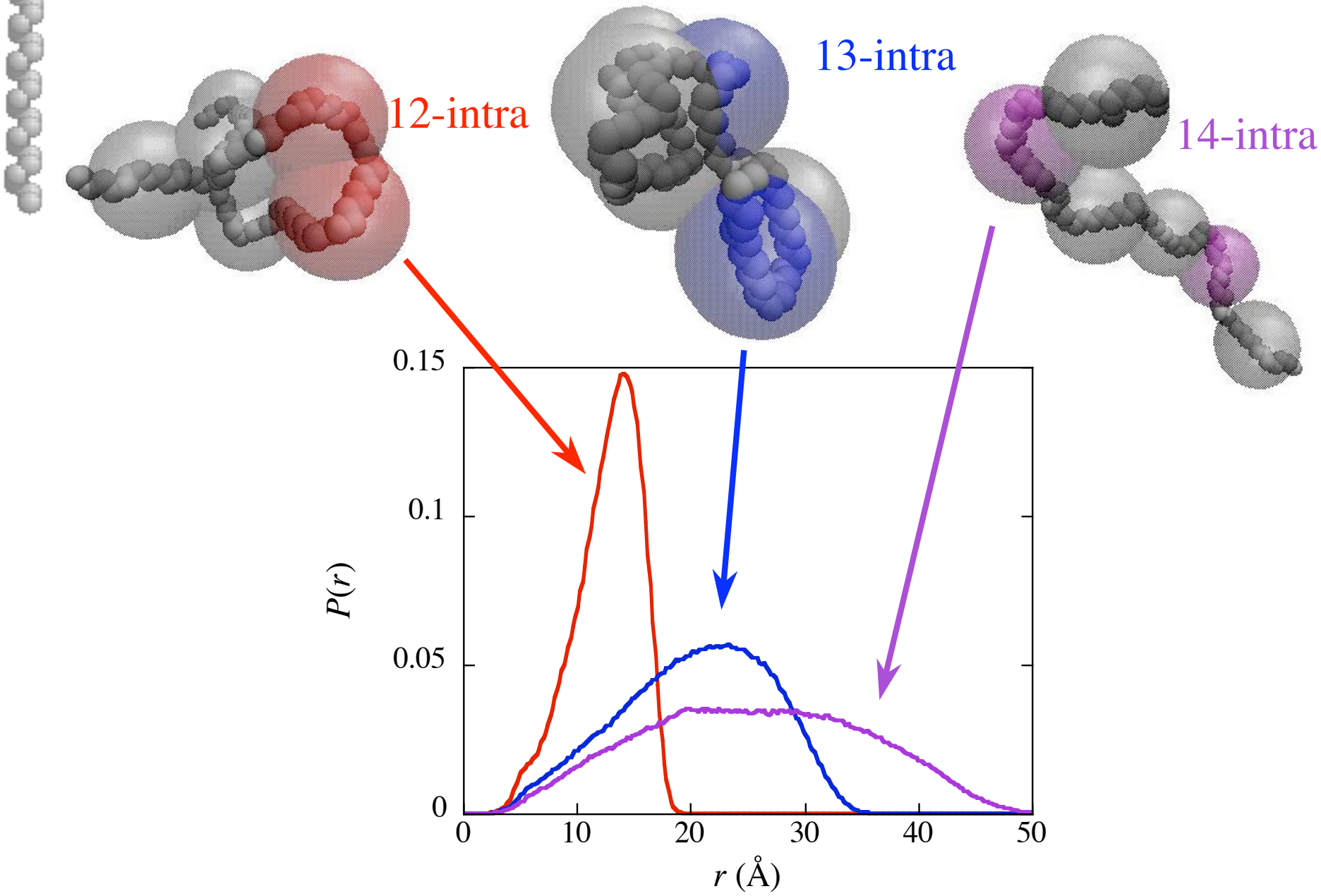
Coarse-graining intermolecular correlations



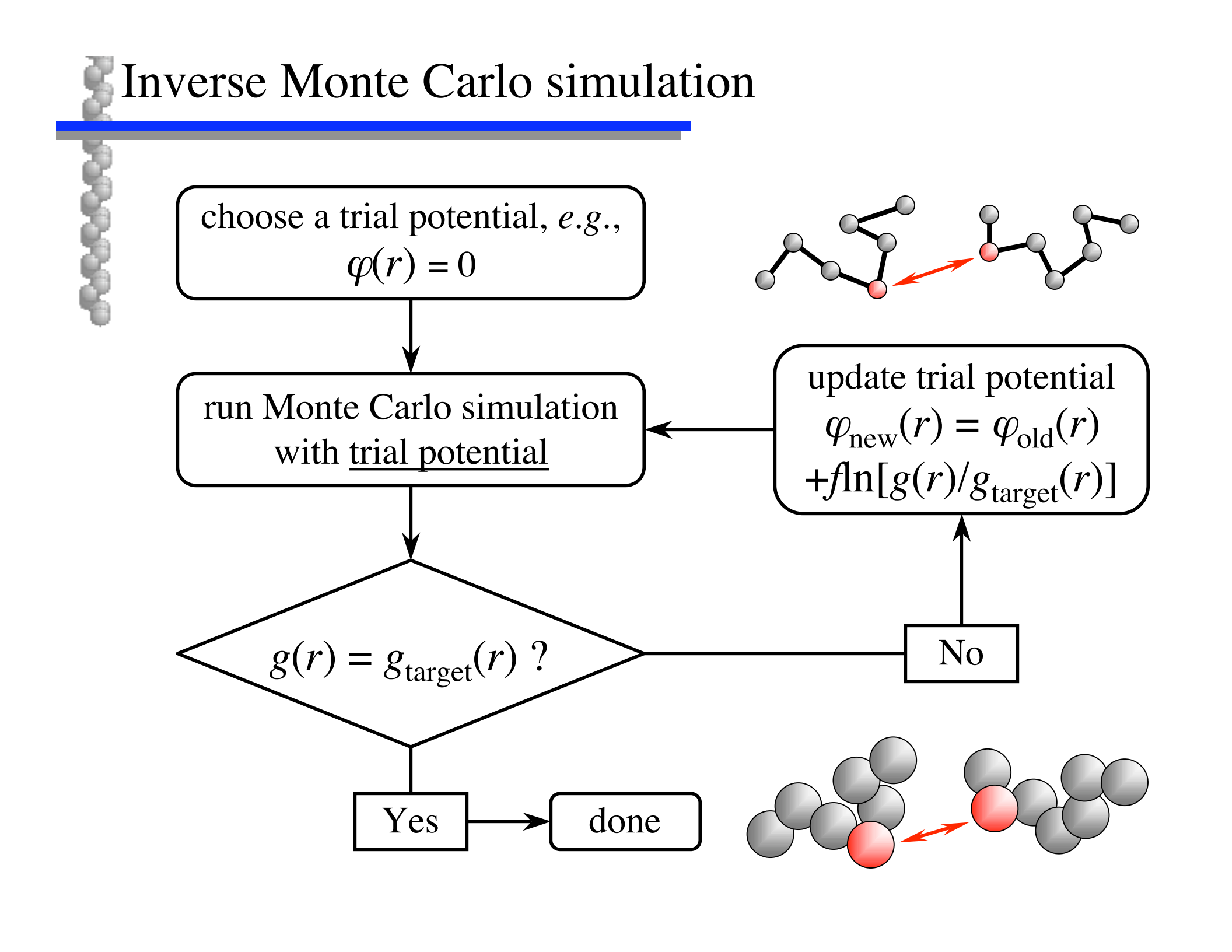


structural details are lost with increasing
the level (n) of coarse-graining process

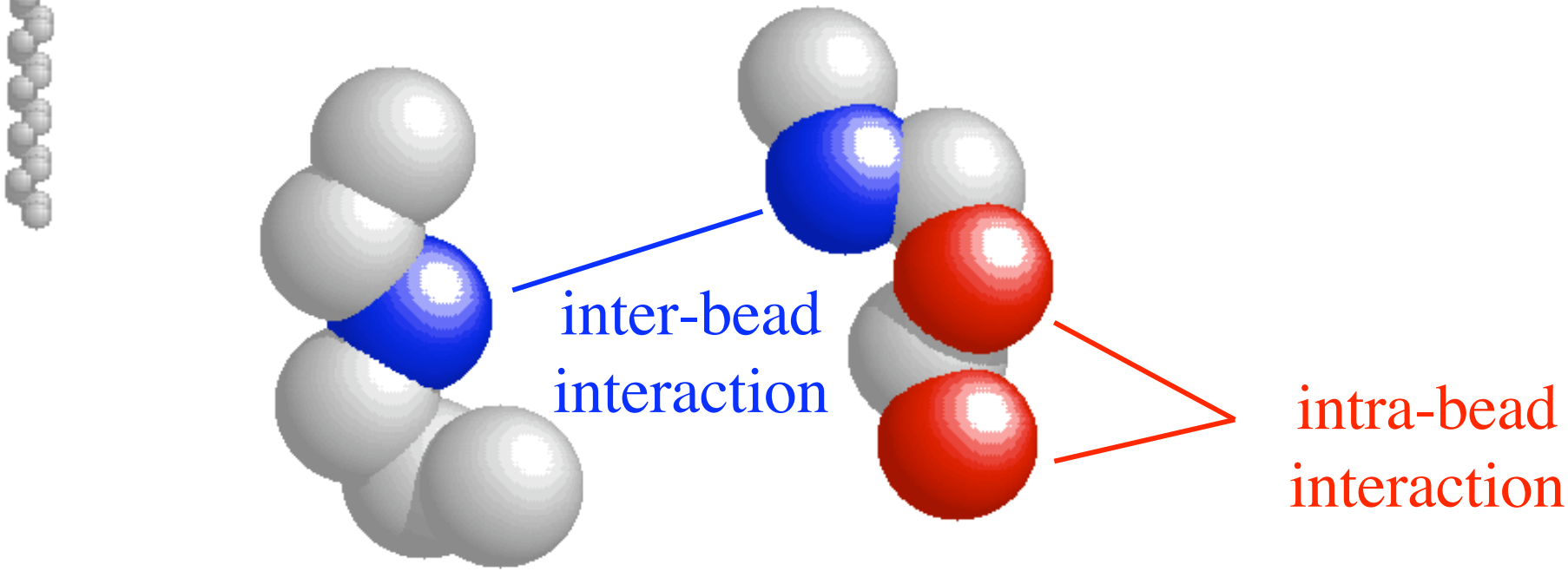
Coarse Graining Intramolecular Correlations



Inverse Monte Carlo simulation



Coarse Grained Potential

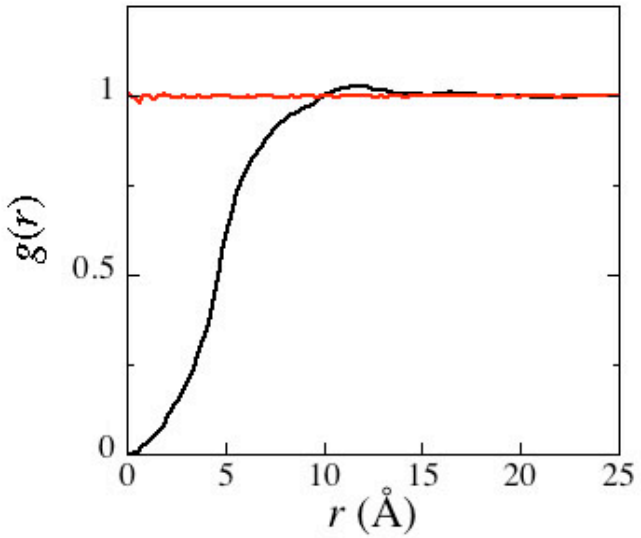


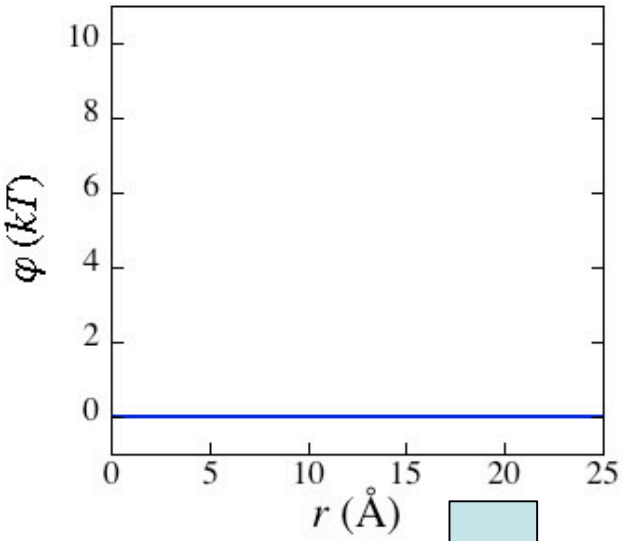
$$E_{\text{total}} = E_{\text{inter}} + E_{\text{intra}}$$

$$= \Sigma_{\text{pairs}} \varphi_{\text{inter}}(r) + \Sigma_{\text{12pairs}} \varphi_{\text{12intra}}(r)$$

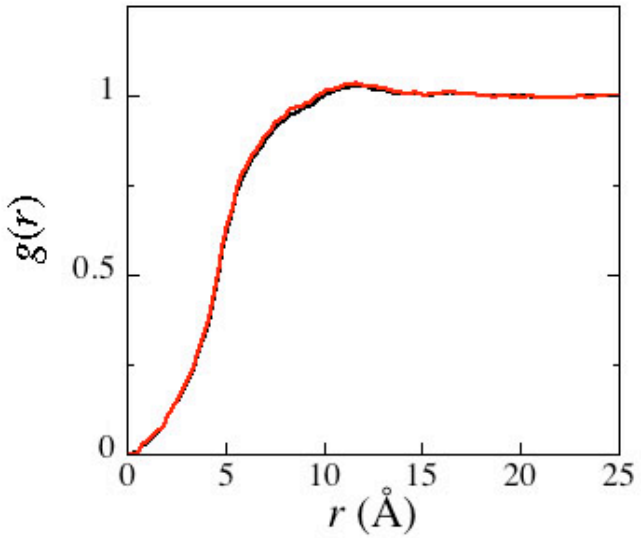
$$+ \Sigma_{\text{13pairs}} \varphi_{\text{13intra}}(r) + \Sigma_{\text{14pairs}} \varphi_{\text{14intra}}(r) + \ldots$$

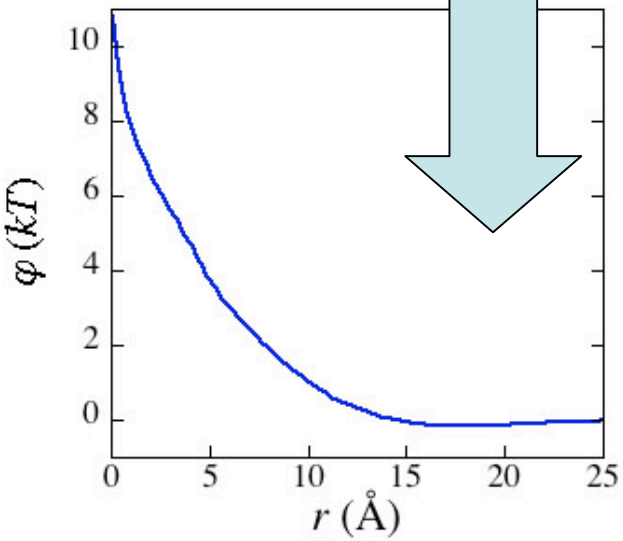
Inter-bead Interactions





before IMC





after IMC

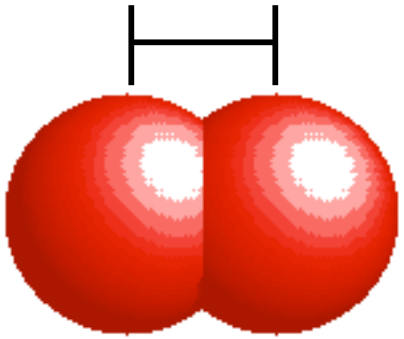
inter-bead radial distribution function

effective interaction potential

Intra-bead Interactions

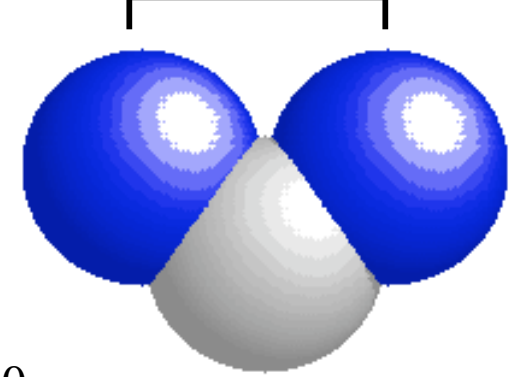
12-intra-bead "bonded" interactions

$\varphi_{12}(r)$



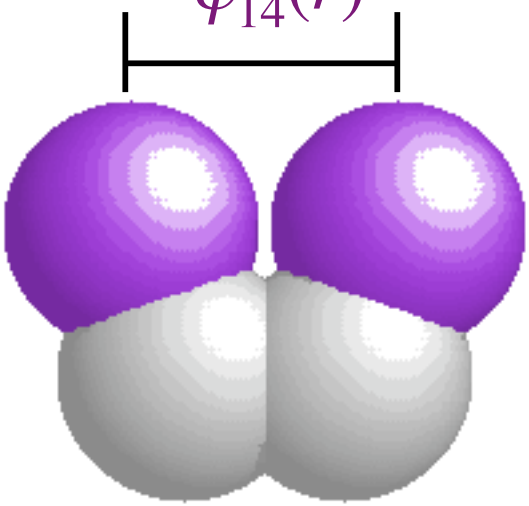
13-intra-bead interactions

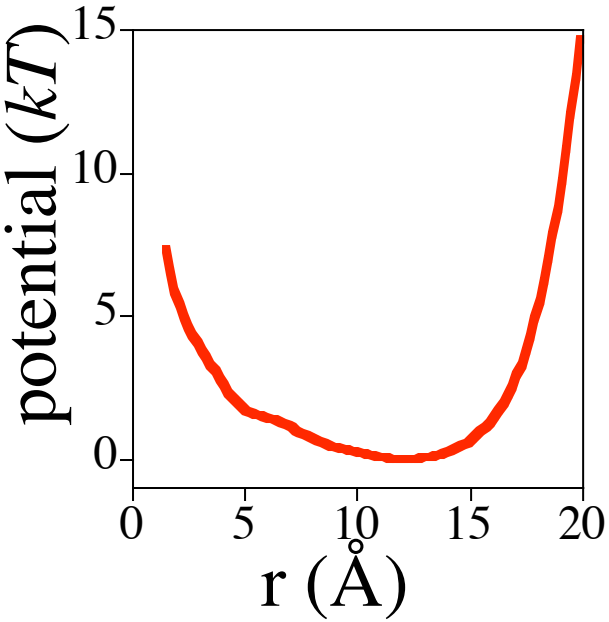
$\varphi_{13}(r)$

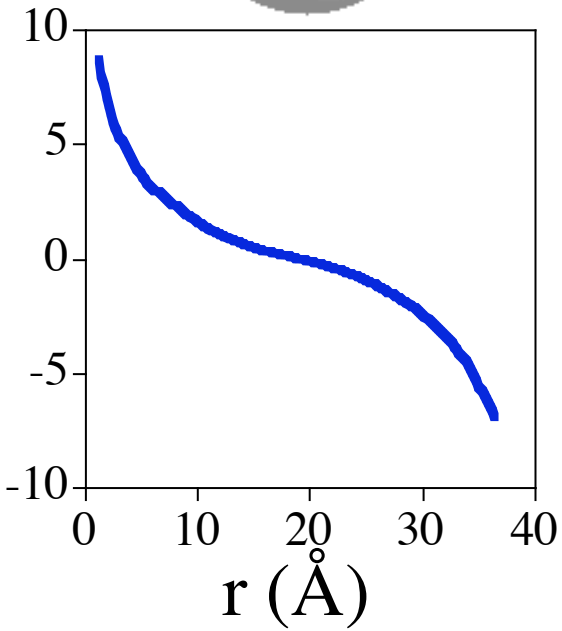


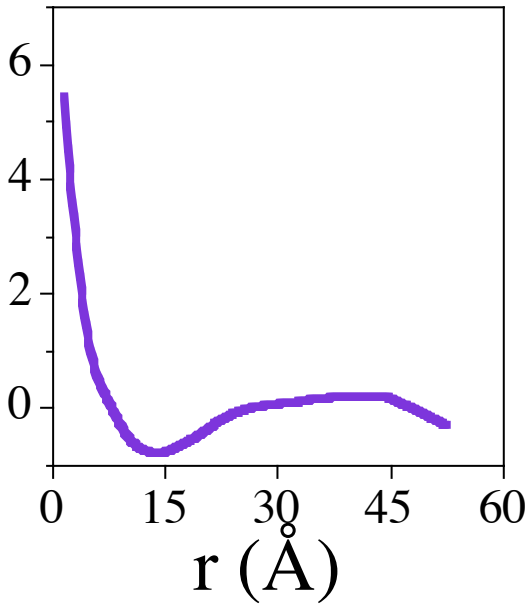
14-intra-bead interactions

$\varphi_{14}(r)$



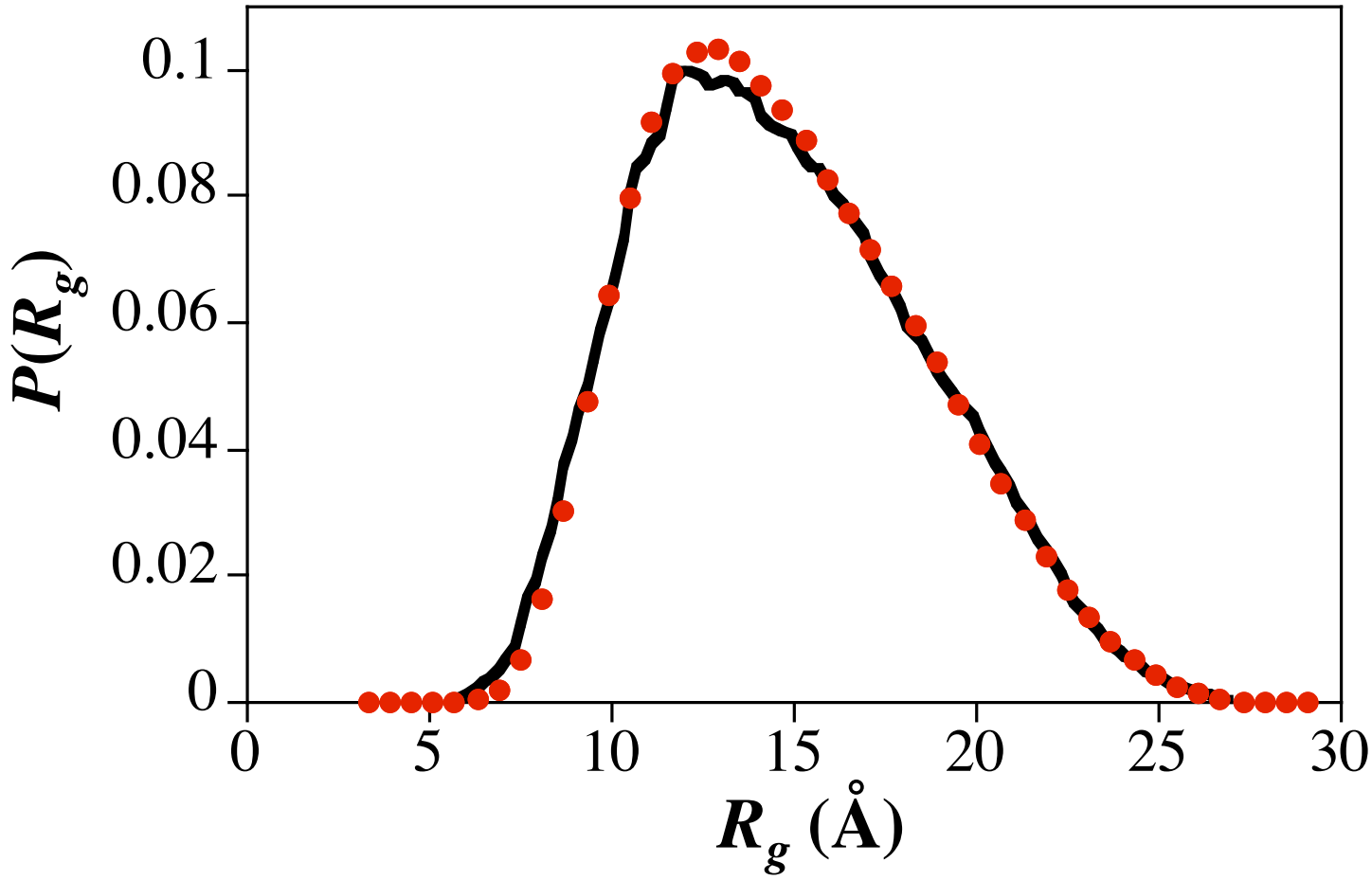






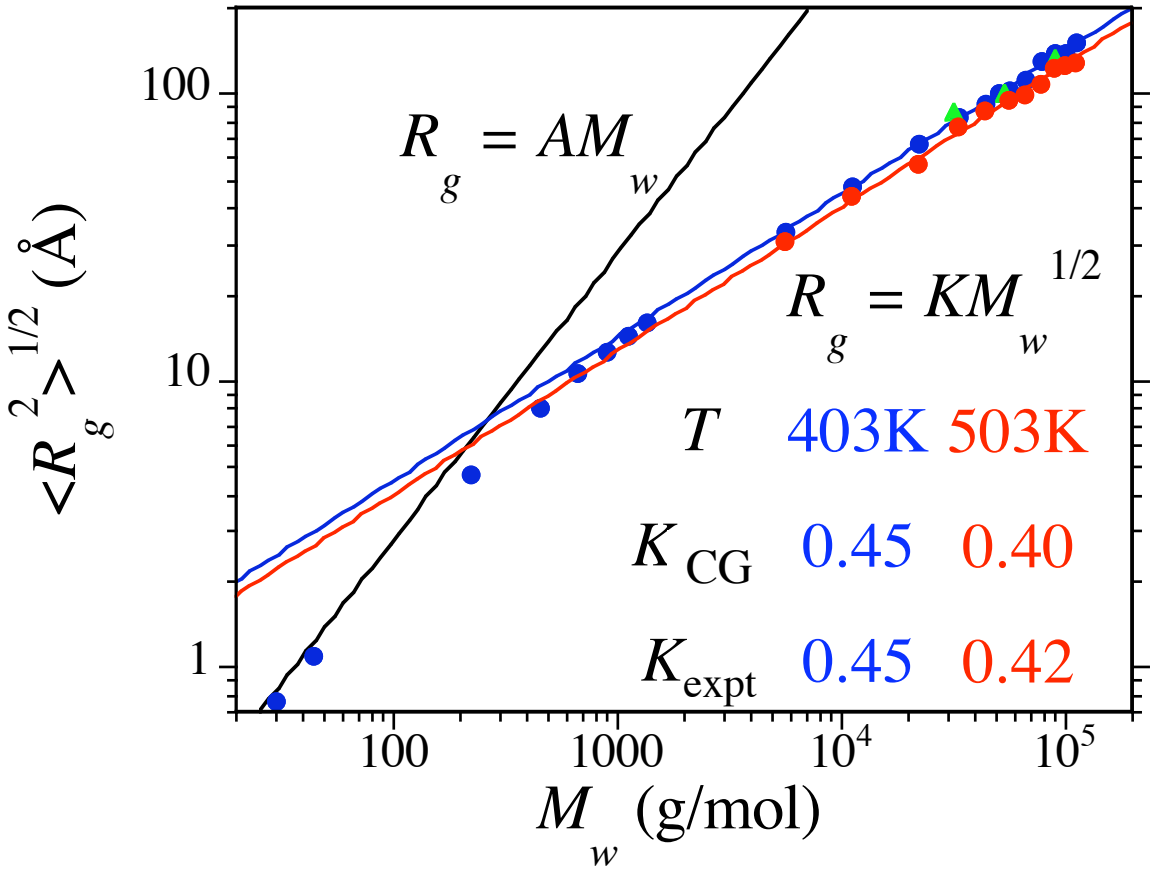
Oligomer conformation distribution

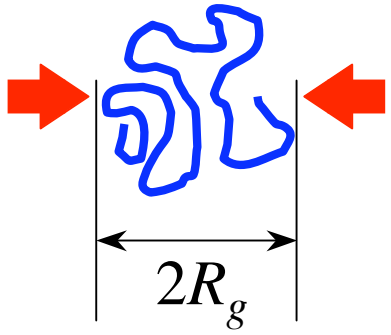
radius of gyration distribution for C96



CG method reproduces conformational statistics of molecular oligomers

Radius of Gyration and Effect of Temperature

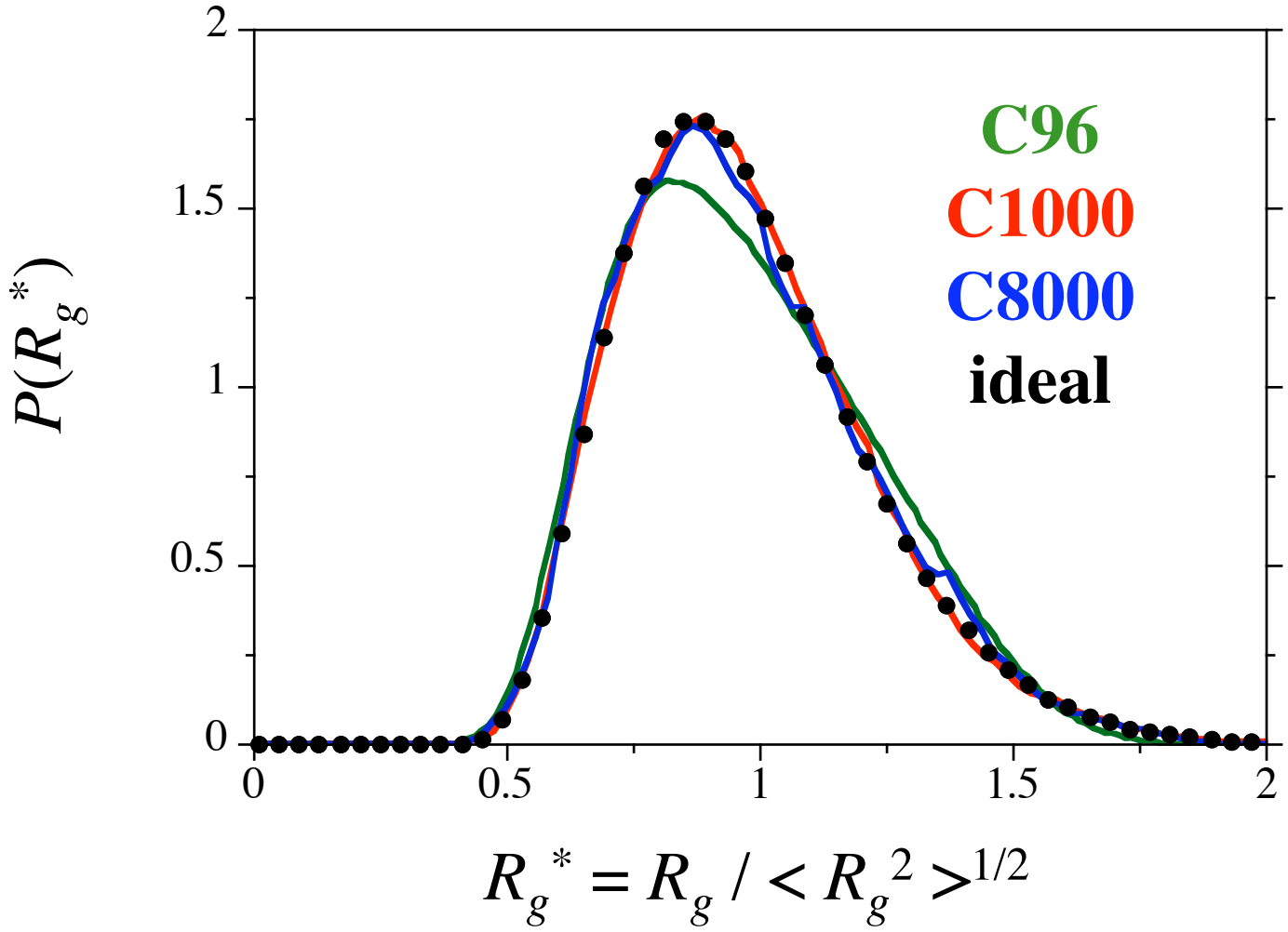




excellent agreement with experiment

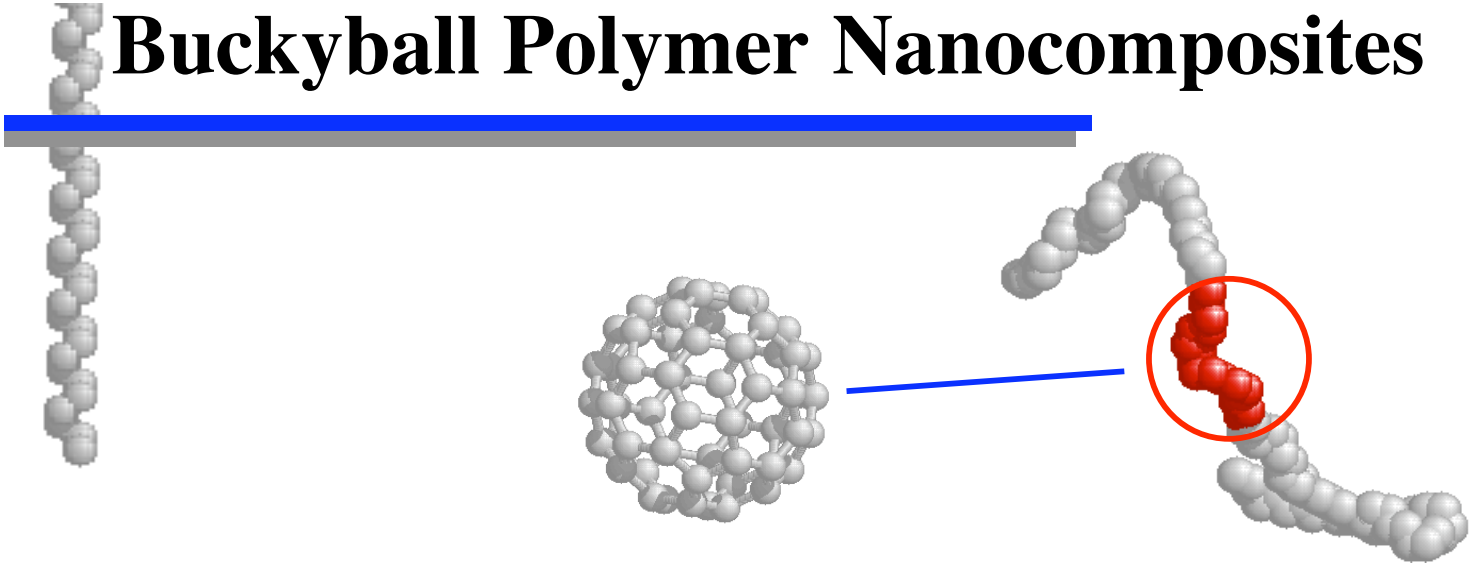
Polymer Conformation Distribution

radius of gyration distribution (403K)

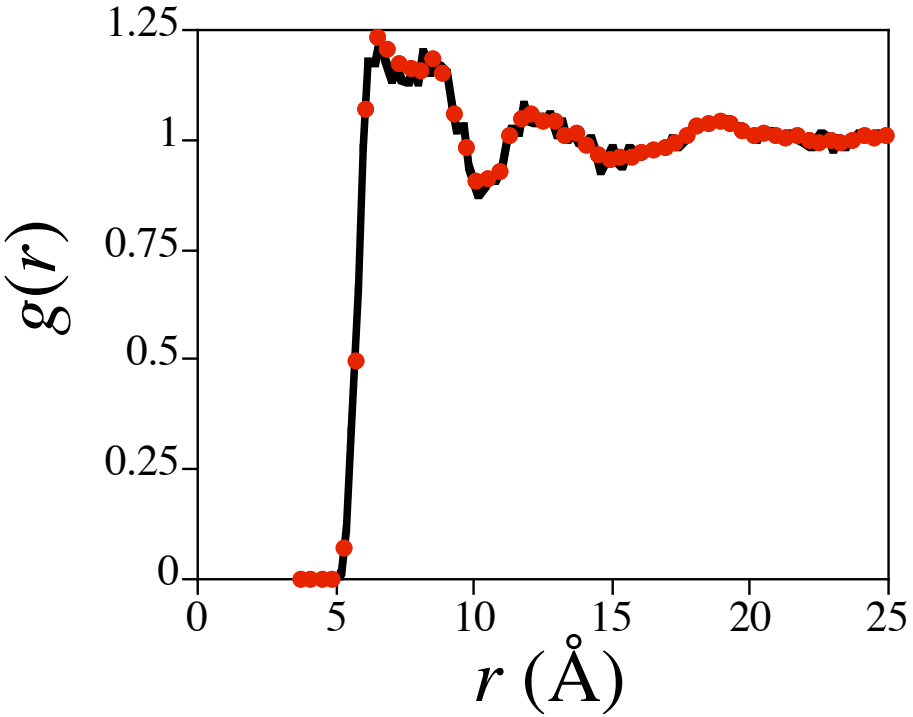


polymer conformational space efficiently explored

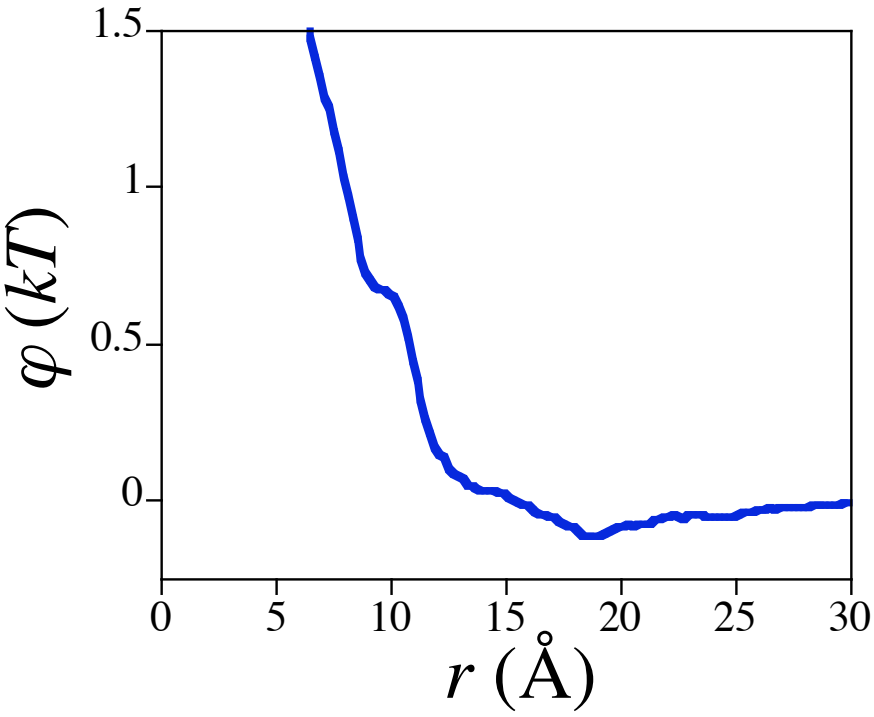
Buckyball Polymer Nanocomposites



bead-ball distribution

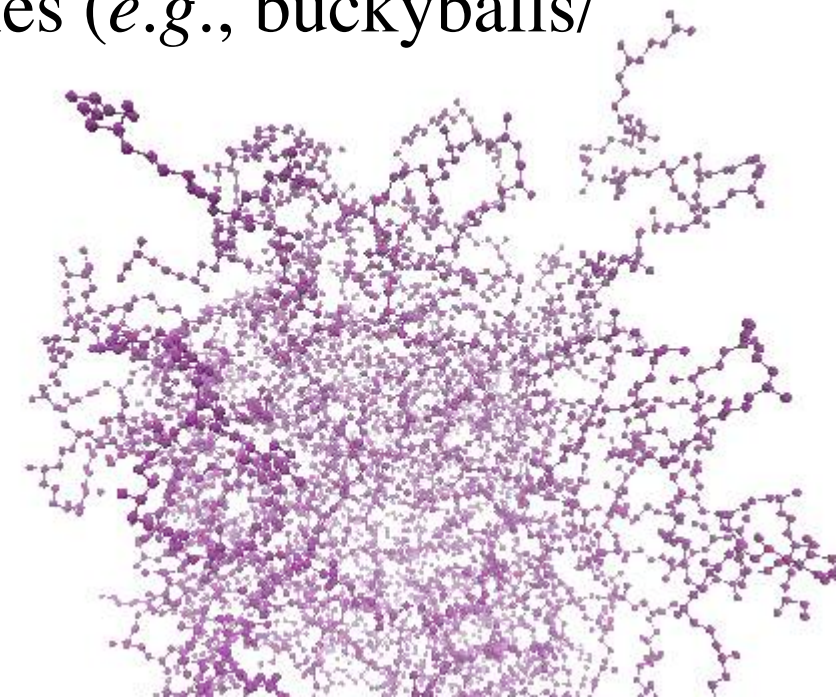


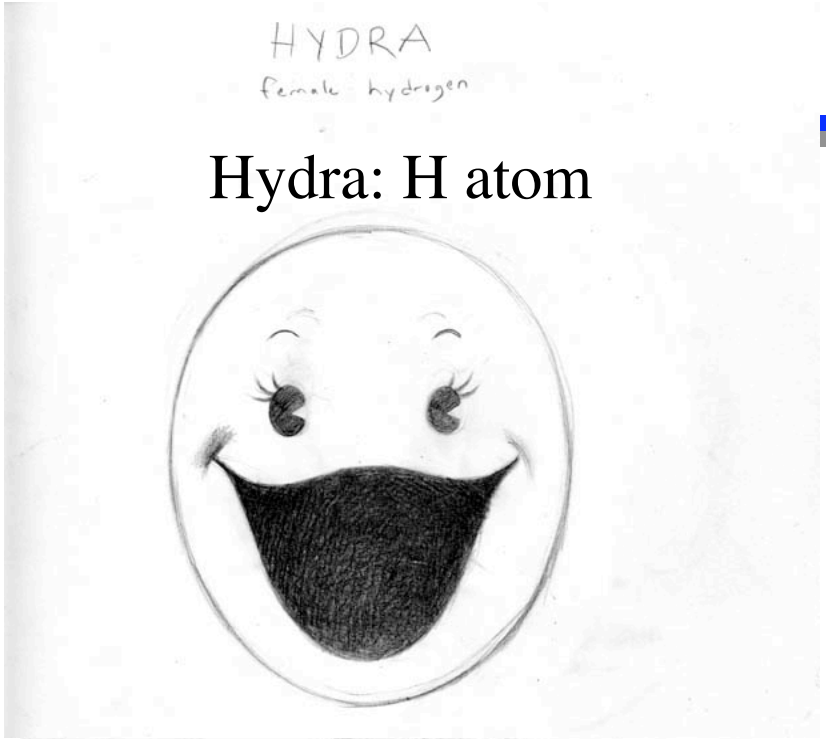
bead-ball interaction



Conclusions

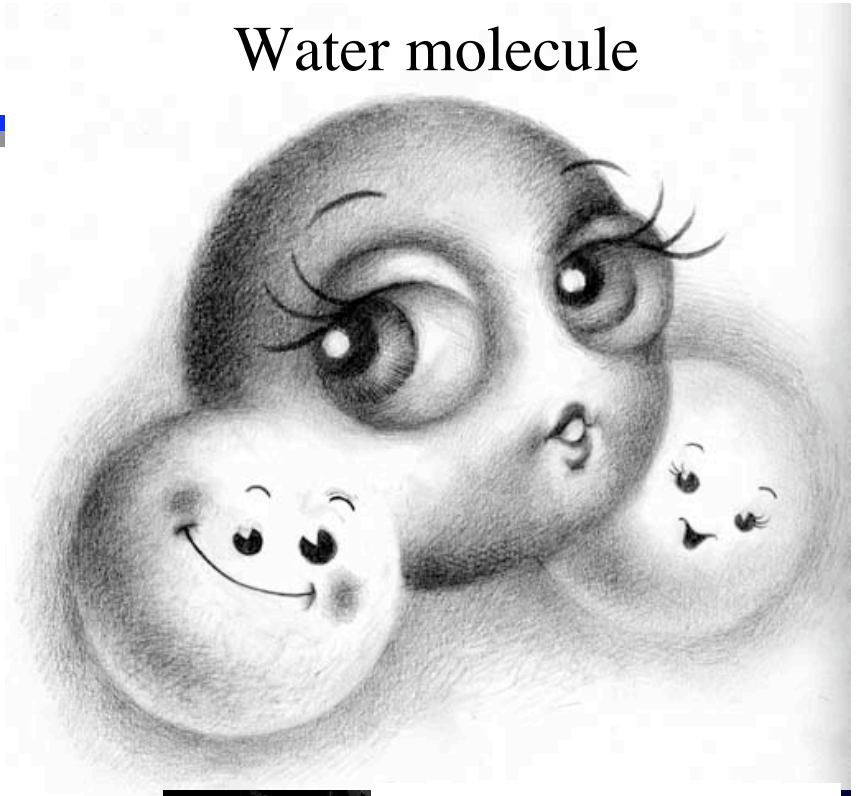
- CG method maps molecular scale correlations to coarse-grained potentials
- Coarse grained potential simpler than molecular potential and can be extended to polymer simulations while preserving molecular identity
- Not limited to polymeric species (*e.g.*, buckyballs/ nanocomposites)
- **Path Forward**
  - Polyolefin blends
  - Block copolymer assembly
  - Dynamics?

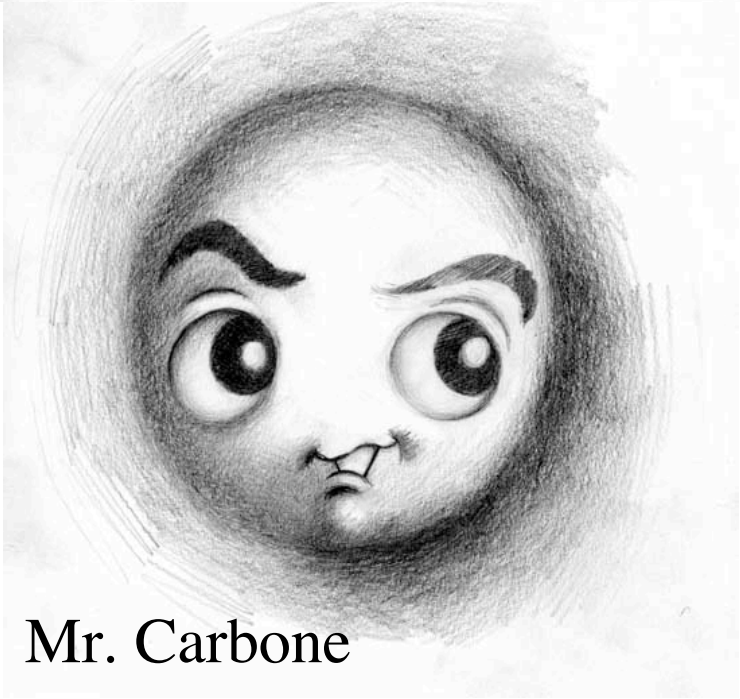




Hydra: H atom

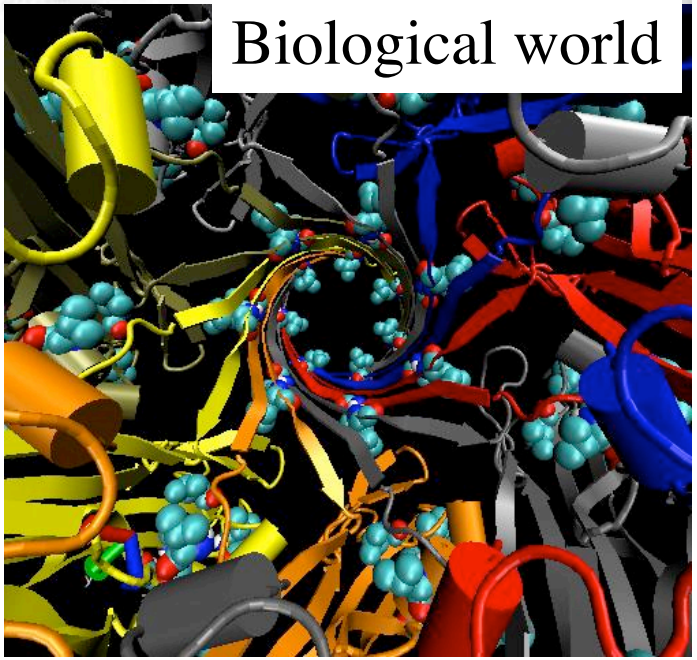
Water molecule

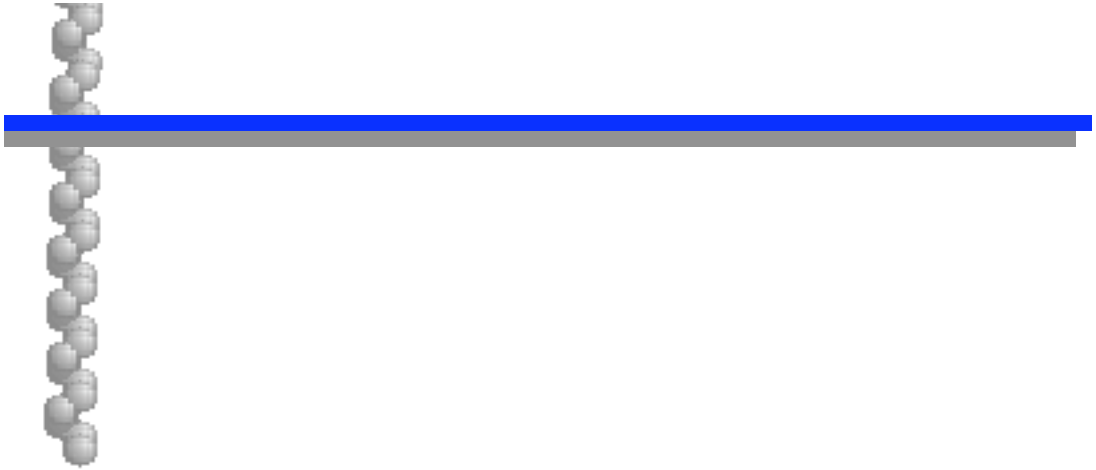




Mr. Carbone

Biological world





Thank you!