Applications to Polymers

Development of quantitative (?) coarse-grained simulation models for polymers
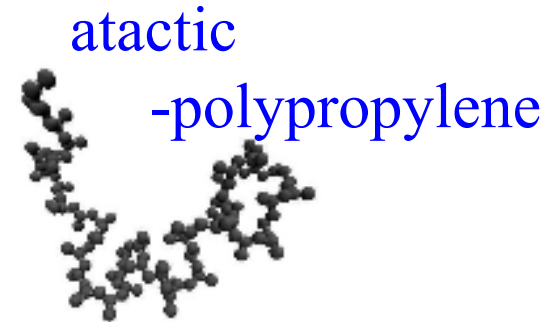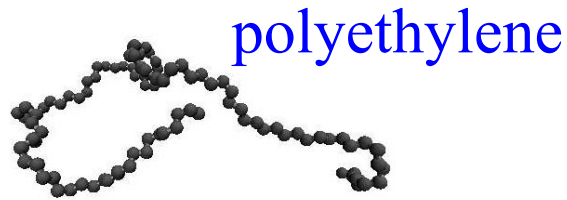
Shekhar Garde & Sanat Kumar (Columbia)

Rensselaer Polytechnic Institute

Graduate students: Harshit Patel & Sandeep Jain
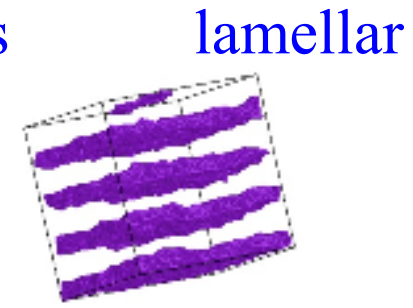Collaborator: Hank Ashbaugh,Tulane Univ.

Our Motivation
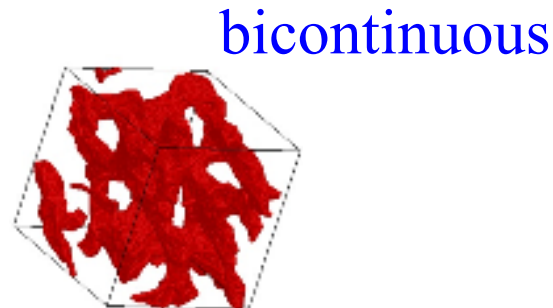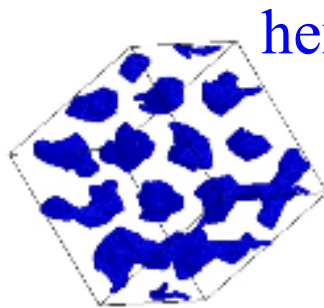
- Polymer blend phase behavior
  - Miscibility/immisciblity of polyolefins

polyethylene

atactic -polypropylene

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

hexagonal   bicontinuous   lamellar

Hierarchy of Length and Time Scales

molecular scale

polymer coil

polymer melt/continuum

persistance length ~10Å

bond length ~1Å

10^{-15} to 10^{-12} sec

~ 100 Å

10^{-8} to 10^{-4} sec

>> 100 Å

$O(1\text{sec})$
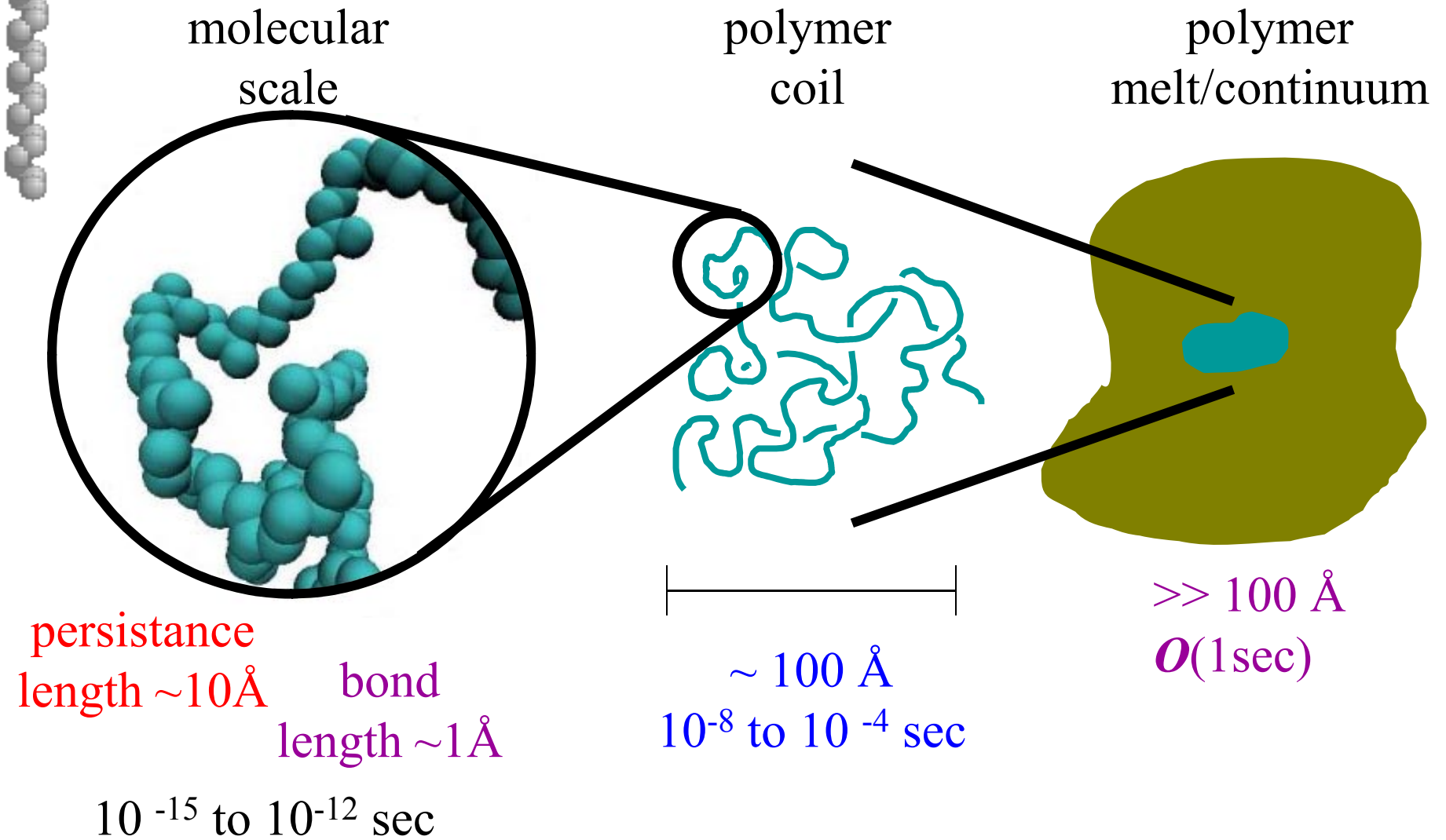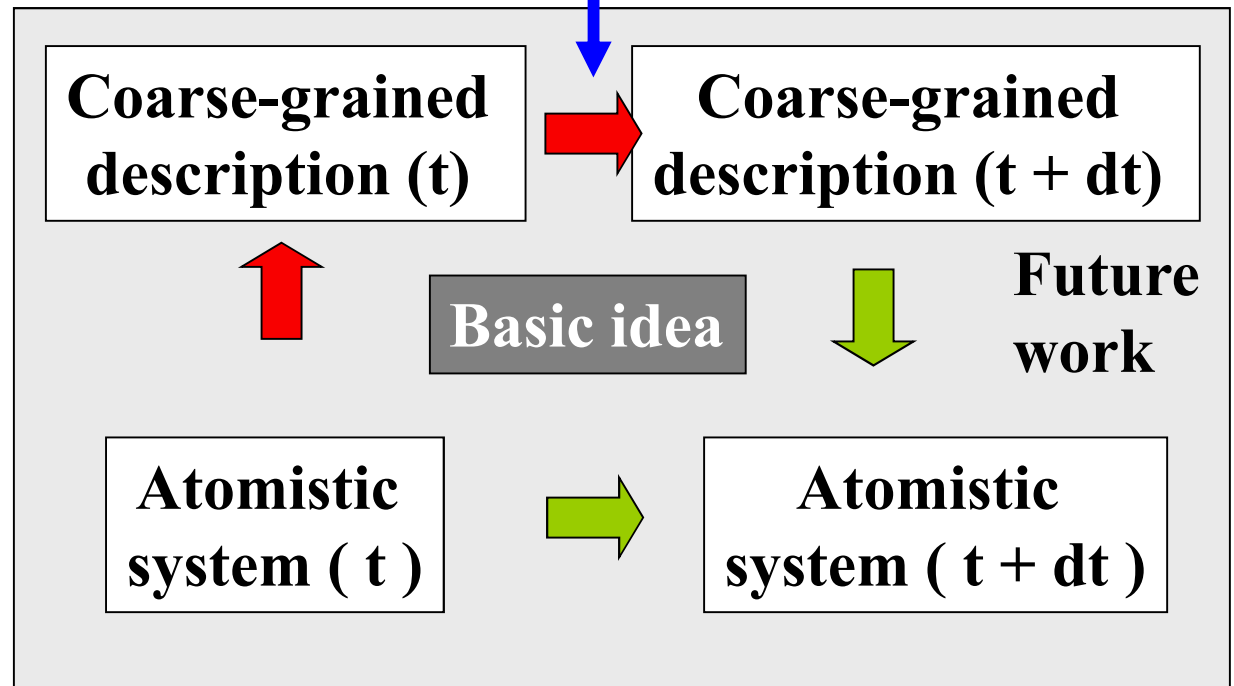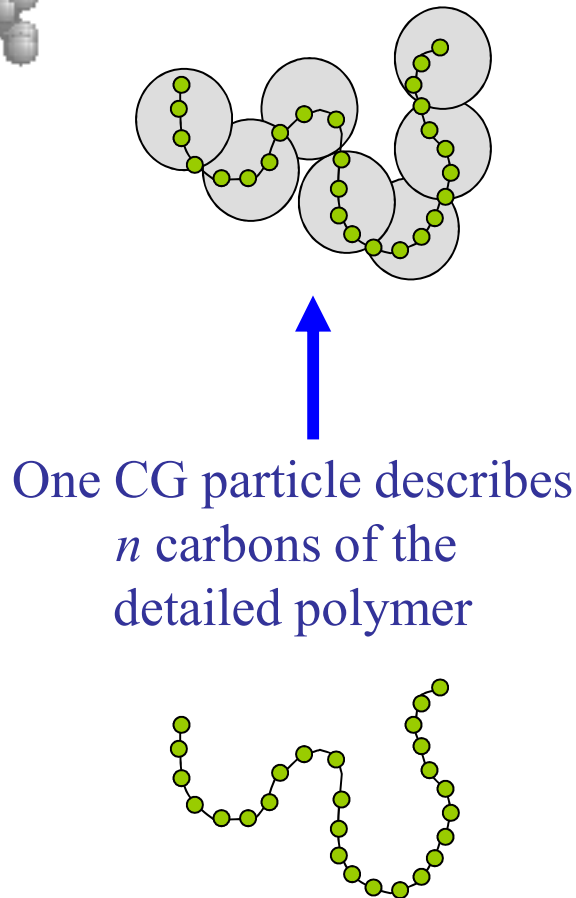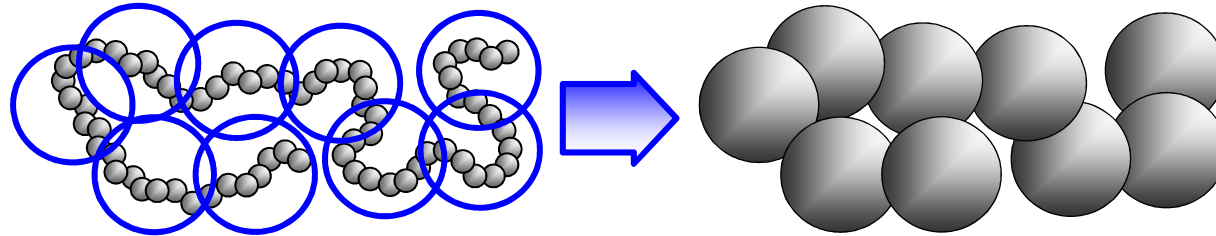
Coarse-graining of Polymer Simulations

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

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

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

Coarse-grained description (t)	**Coarse-grained description (t + dt)**

Basic idea

Future work

|	
Atomistic system (t)	**Atomistic system (t + dt)**

Coarse-graining method

- Perform molecularly detailed simulations of polymers

- Define coarse-grained beads by **grouping N backbone monomers into one**.

- Calculate structural correlations between coarse-grained beads. **CG g(r)**.

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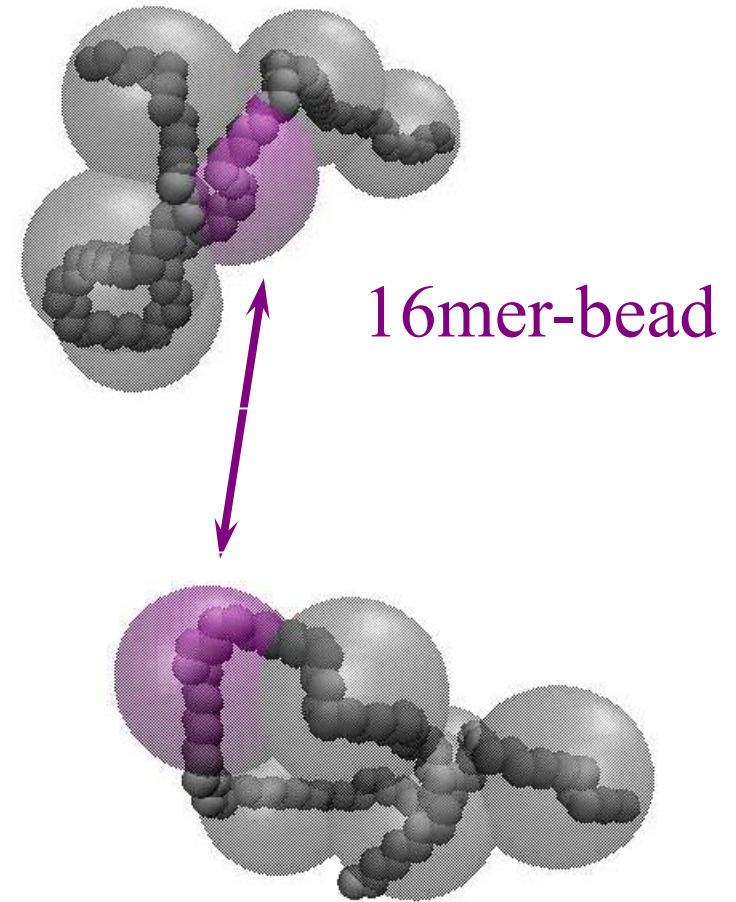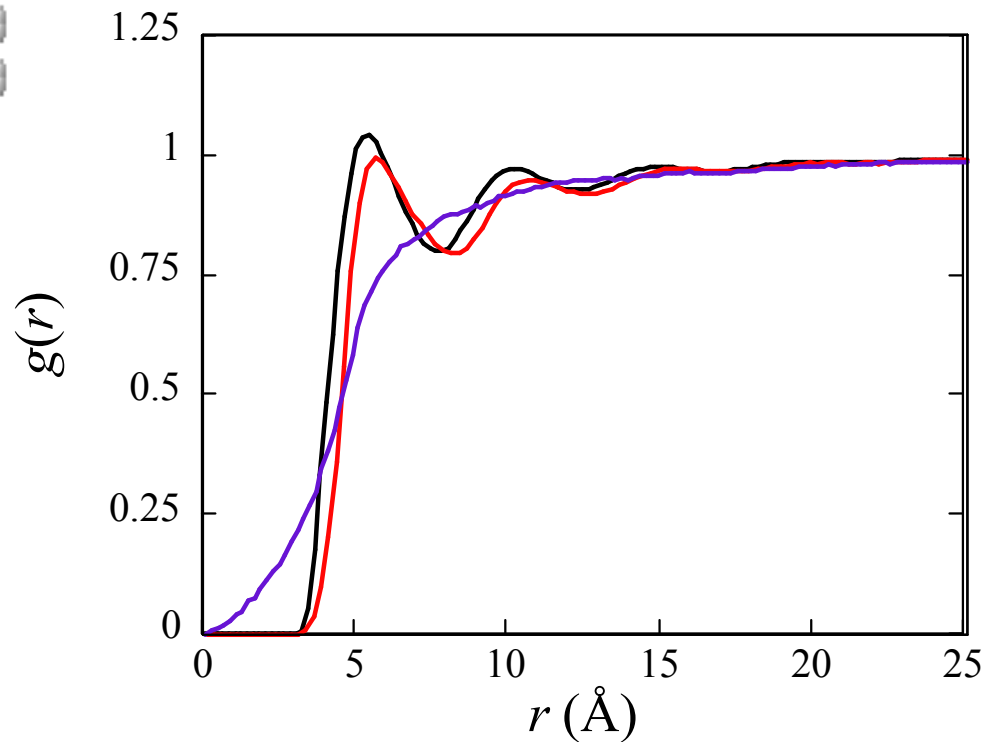
Detailed molecular dynamics simulations

- Classical molecular dynamics

- *n*-alkanes - **C16 to C96**

    (M. Mondello *et al*. JCP 1998)
Includes united atom, bond-length,
angle, and dihedral terms.

- 50 to 100 chains

- T = 403K   P = 1 atm

- time = 5 to 10 ns
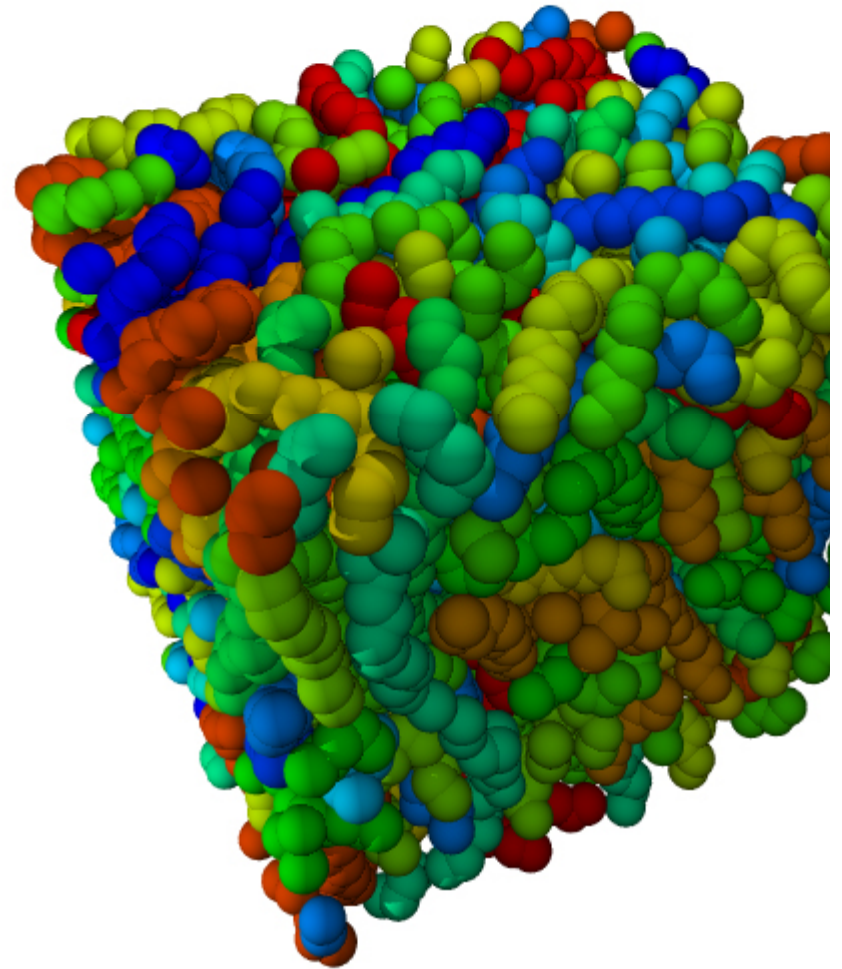
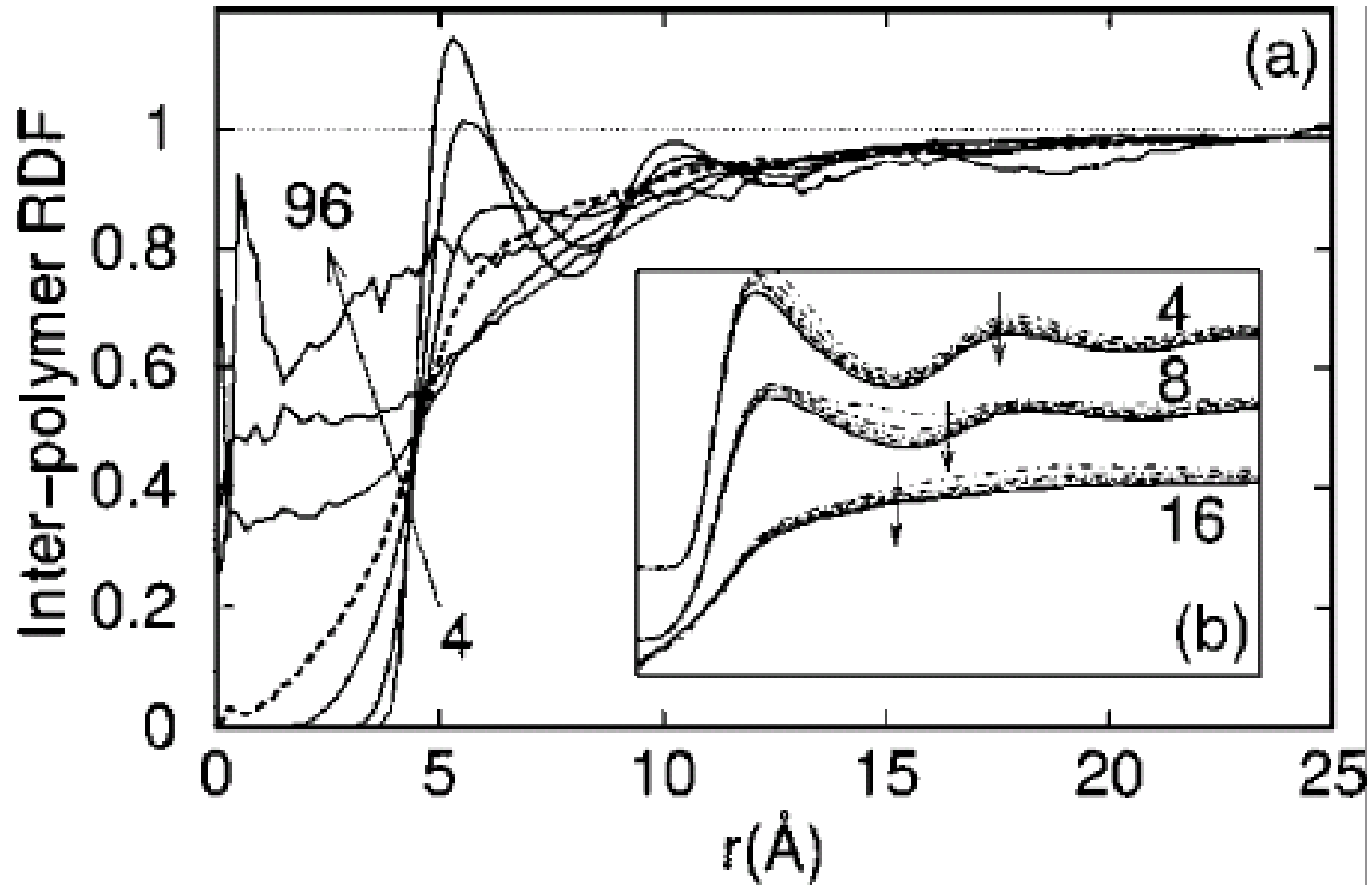# Coarse-graining intermolecular correlations

16mer-bead

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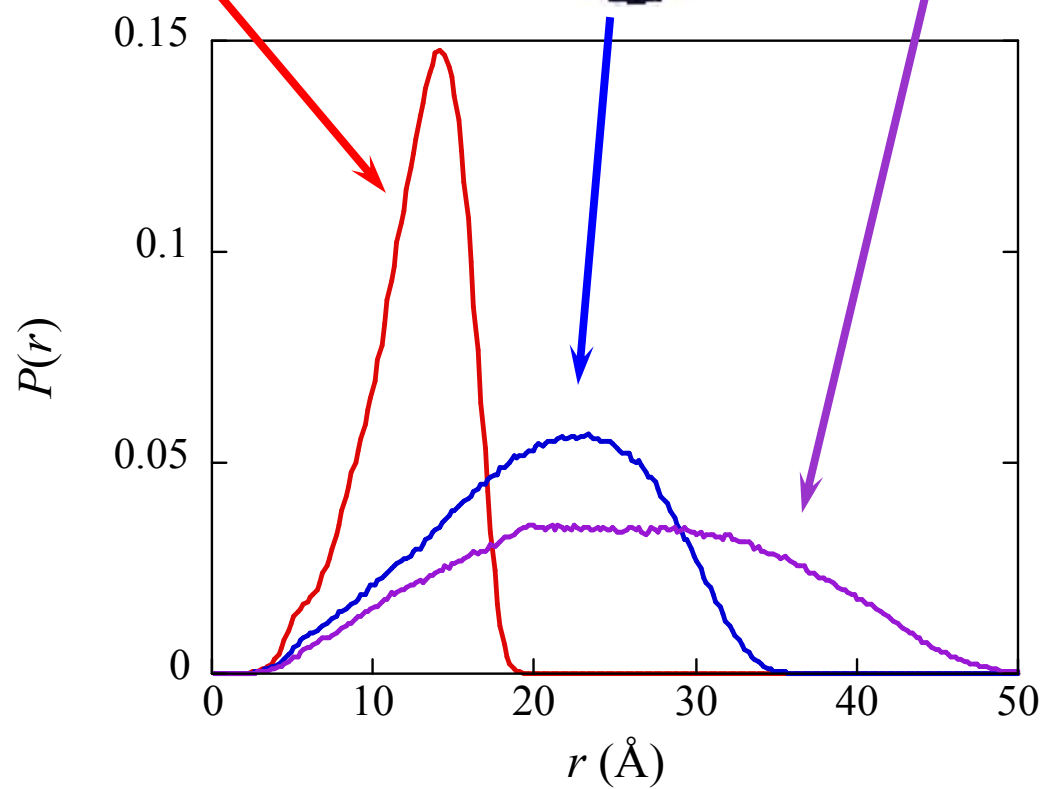the level (N) of coarse-graining process

CG g(r)s as a function of the level of CG
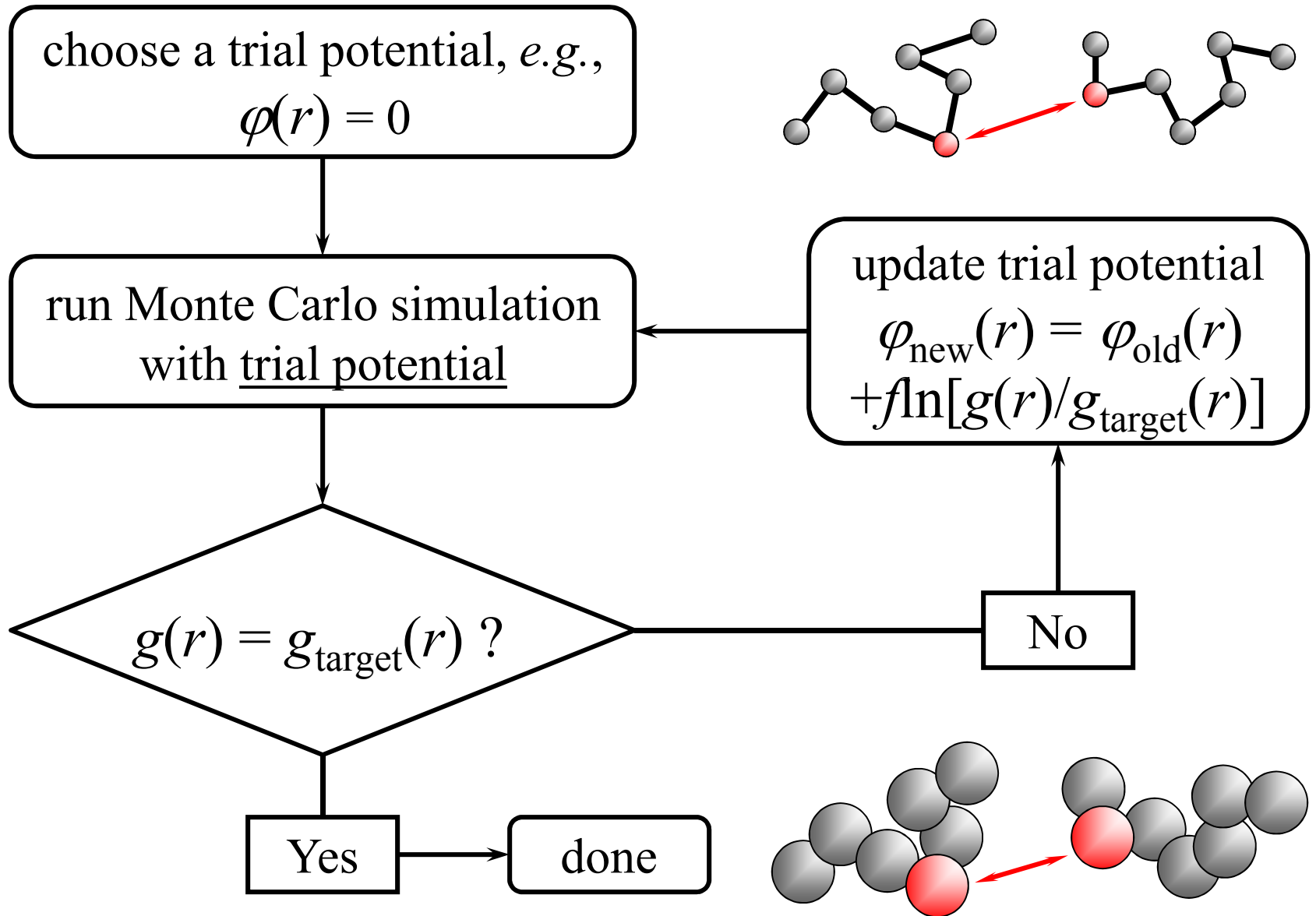
N = 4, 8, 16, 24, 48, 64, 96
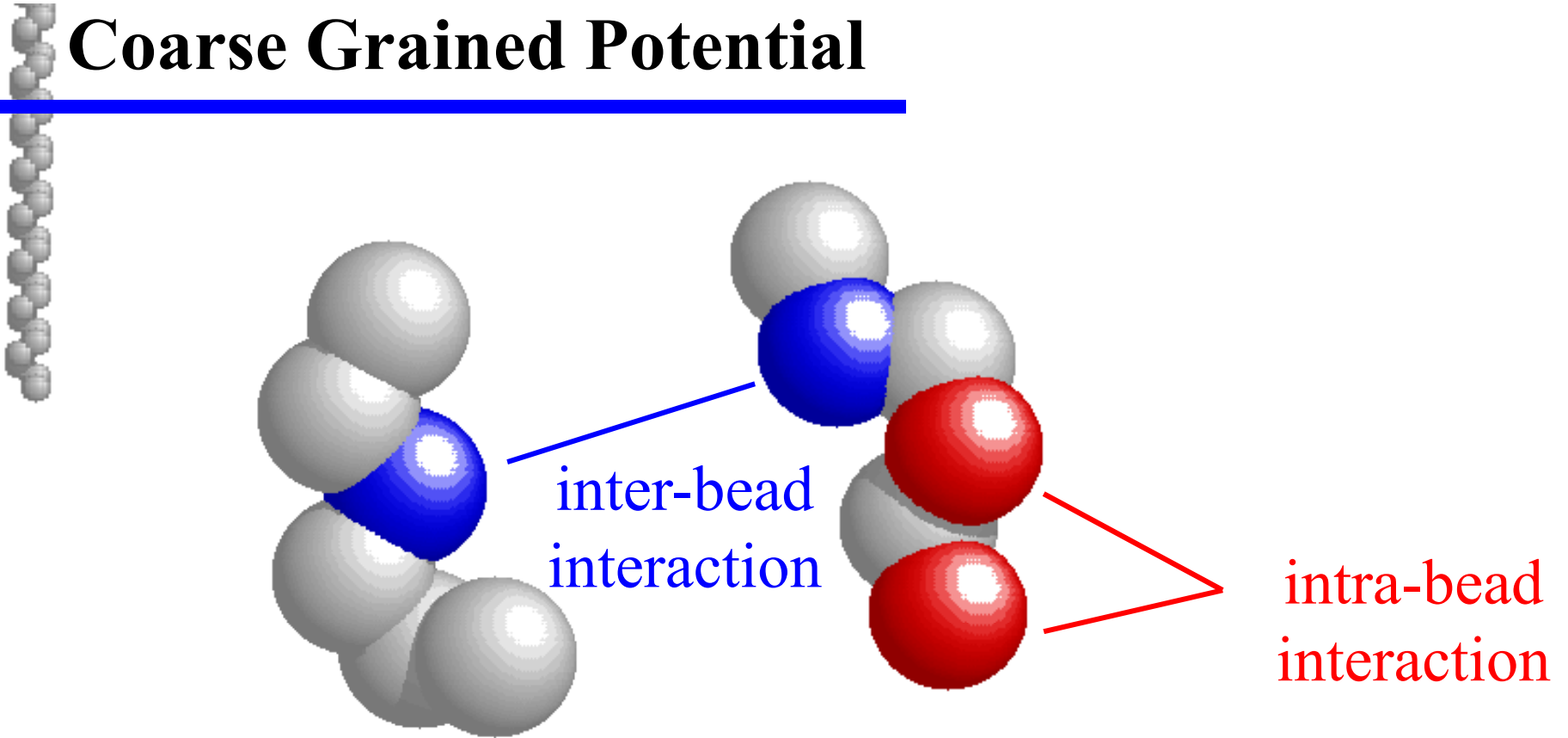
Coarse Graining Intramolecular Correlations
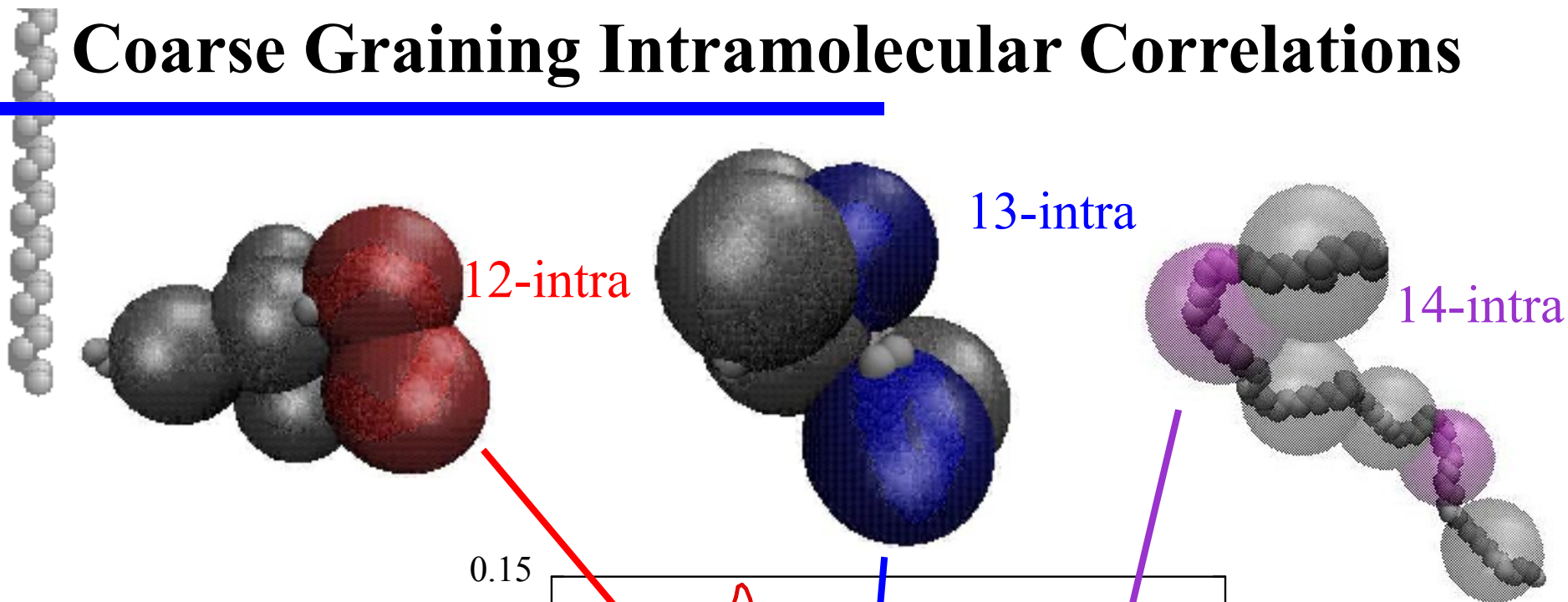
Inverse Monte Carlo simulation

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

run Monte Carlo simulation
with <u>trial potential</u>

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

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

No

Yes → done

Coarse Grained Potential

inter-bead interaction

intra-bead interaction

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

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

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

Inter-bead Interactions
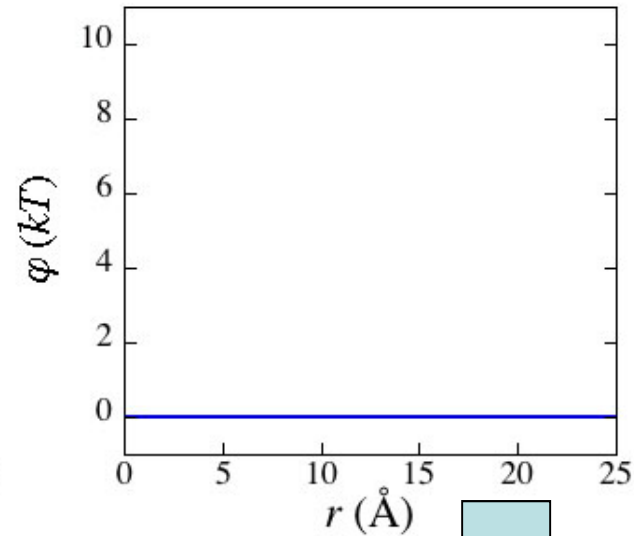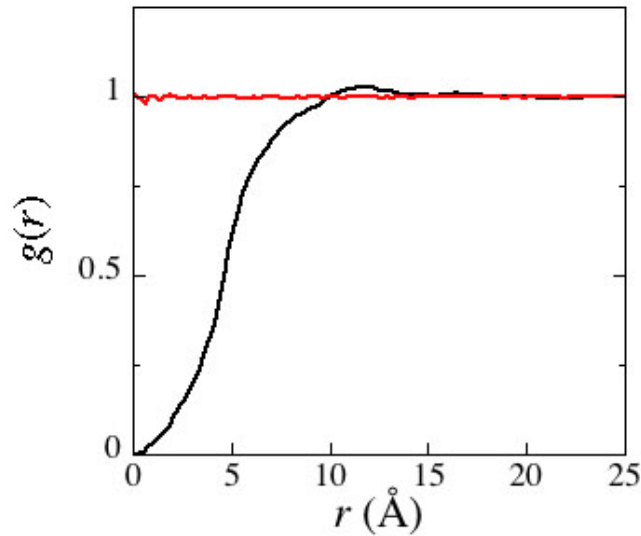
before IMC
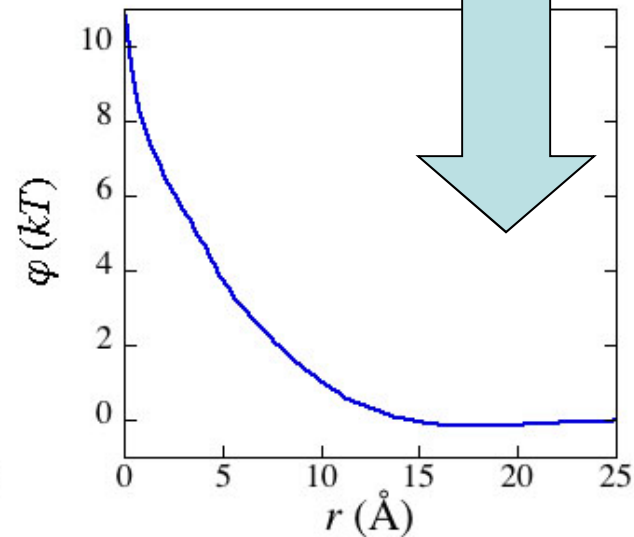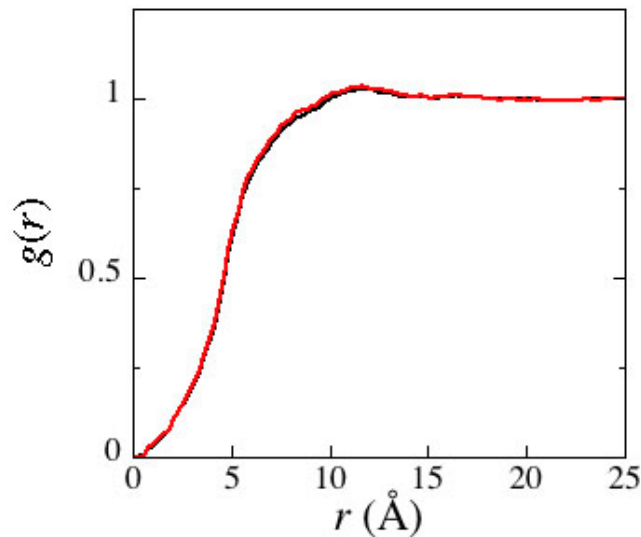
after IMC

inter-bead radial
distribution function

effective interaction
potential

Intra-bead Interactions

12-intra-bead "bonded" interactions
$\varphi_{12}(r)$
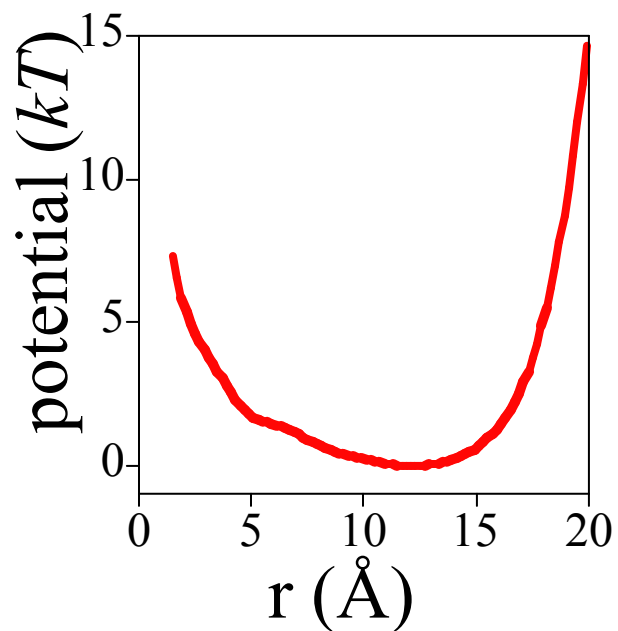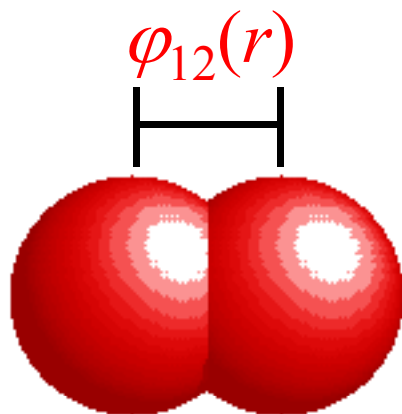
13-intra-bead interactions
$\varphi_{13}(r)$
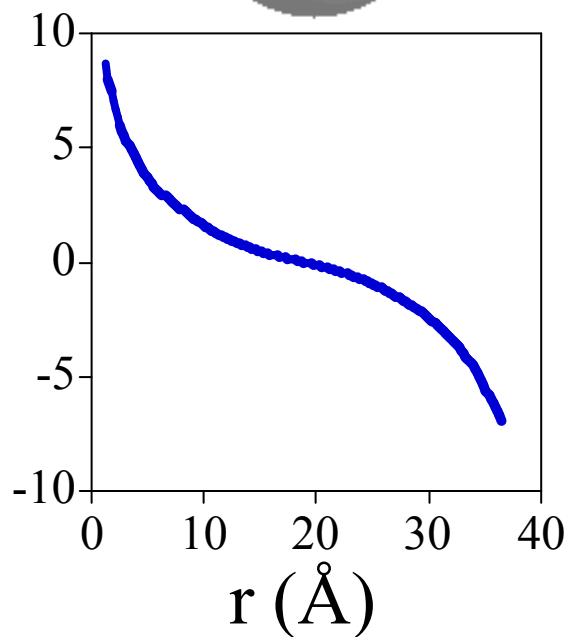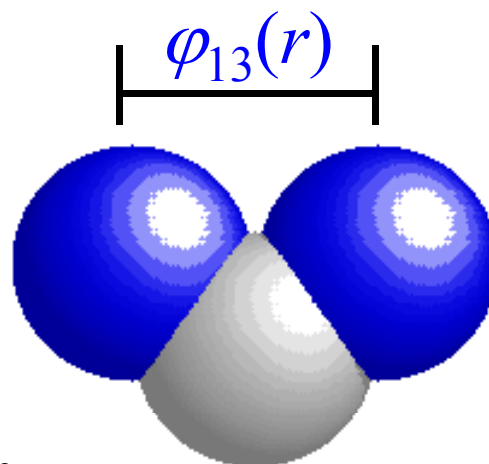
14-intra-bead interactions
$\varphi_{14}(r)$
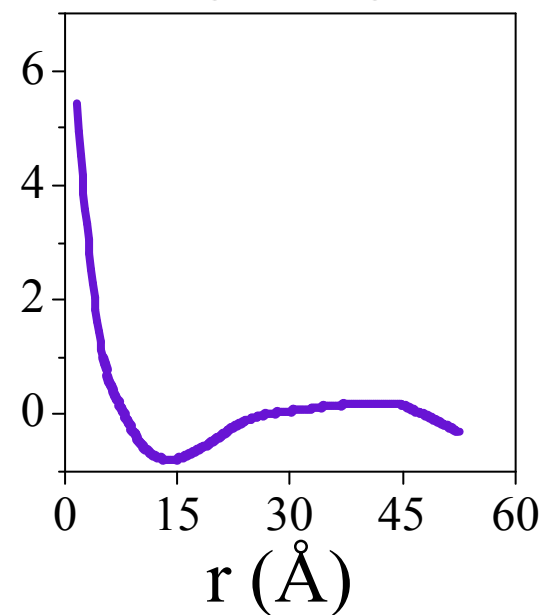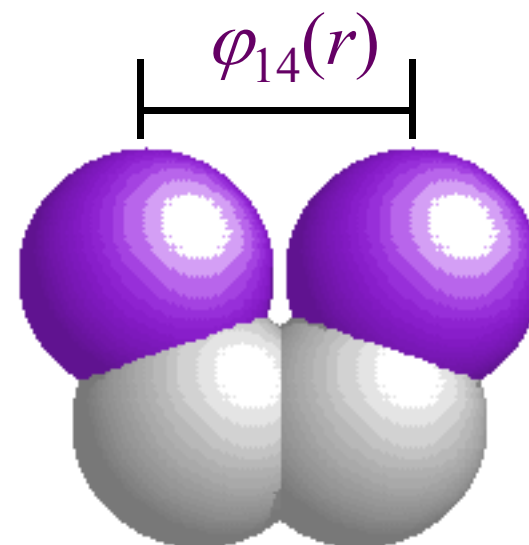
Oligomer conformation distribution

radius of gyration distribution for C96
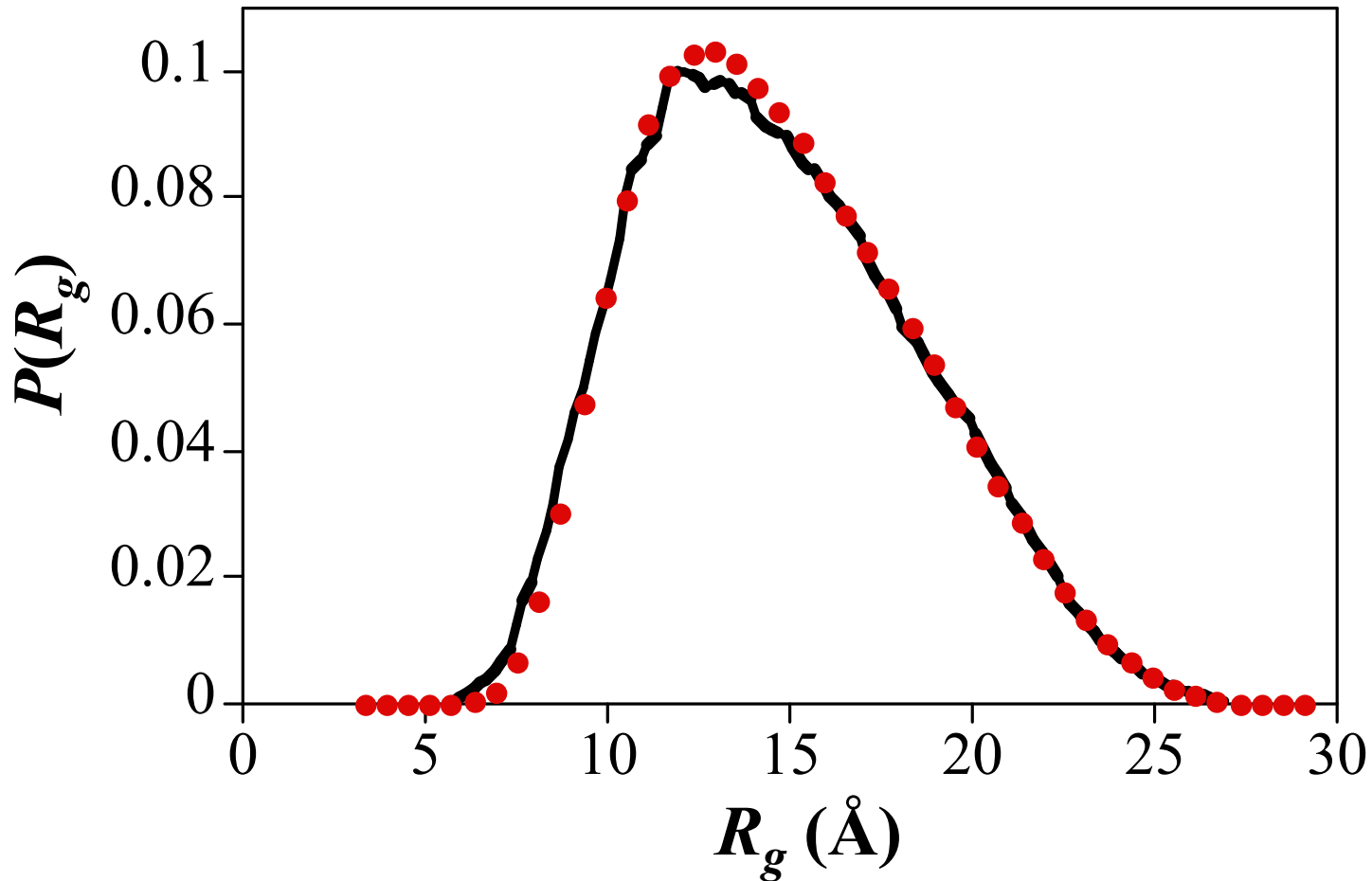
CG method reproduces conformational statistics of molecular oligomers

Radius of Gyration and Effect of Temperature

$$R_g = AM_w$$

$$R_g = KM_w^{1/2}$$

T	403K	503K
K_{CG}	0.45	0.40
K_{expt}	0.45	0.42

$2R_g$
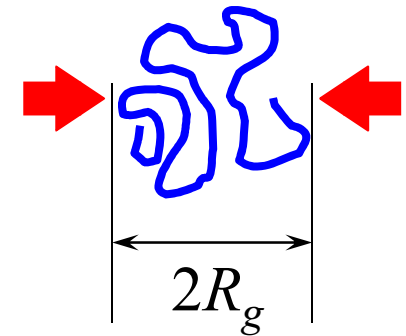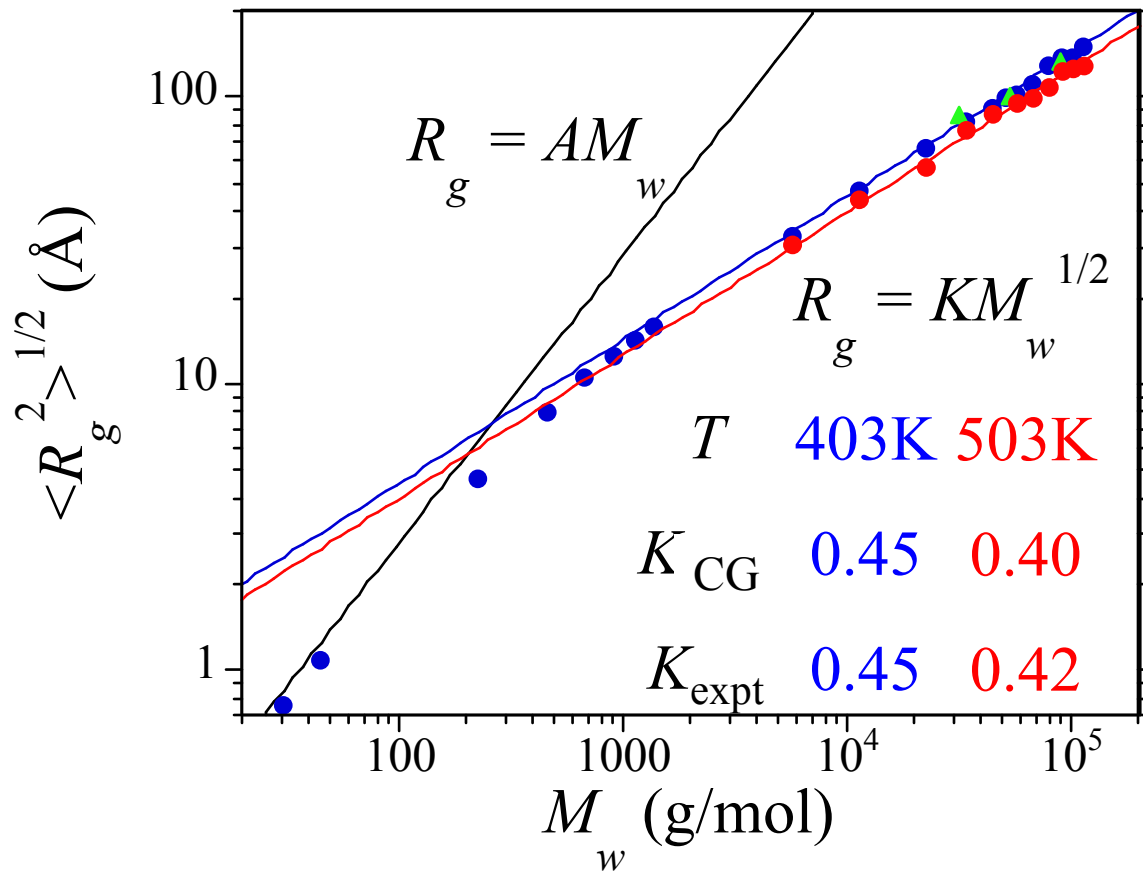
excellent agreement with experiment

Polymer Conformation Distribution

radius of gyration distribution (403K)
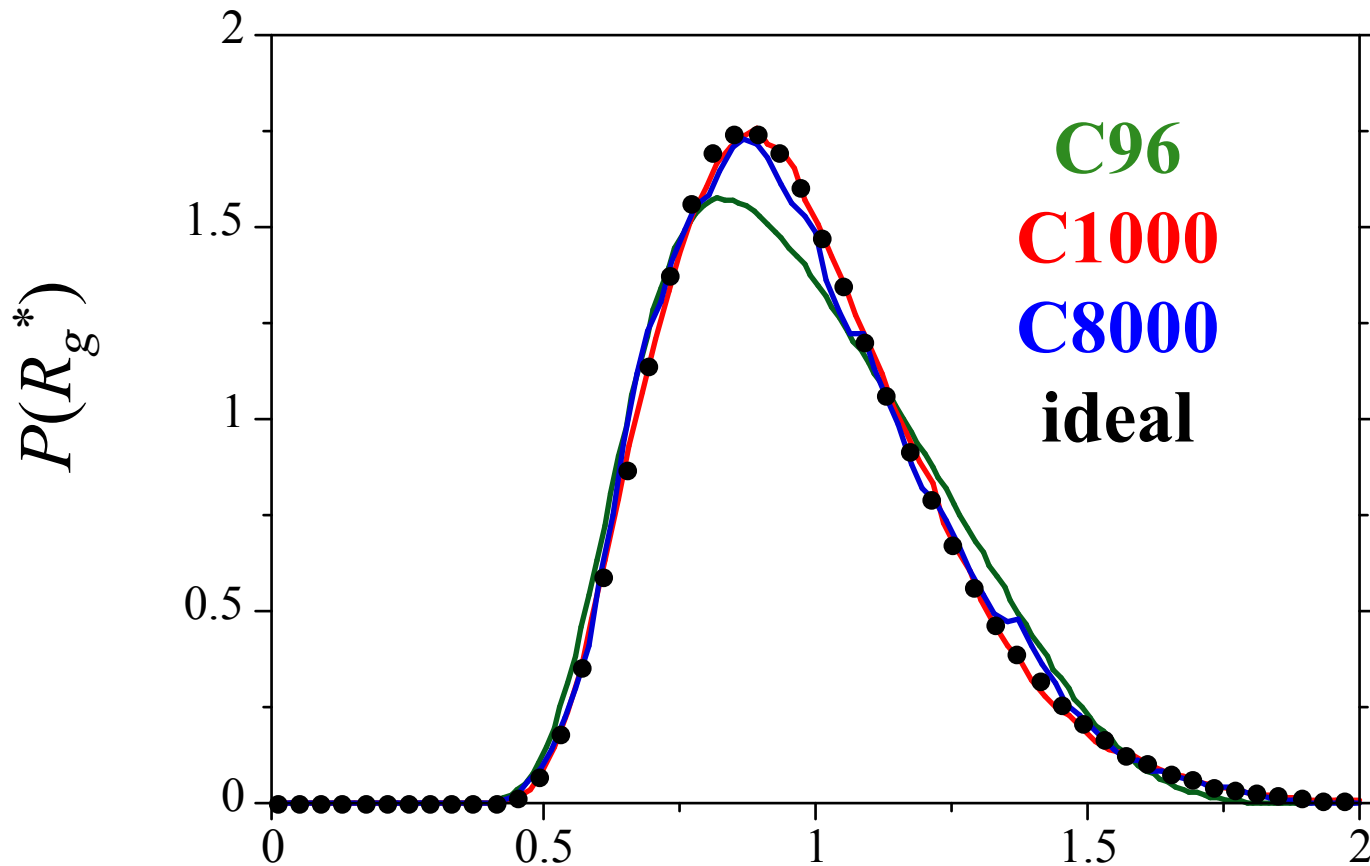
$$R_g^* = R_g / < R_g^2 >^{1/2}$$

polymer conformational space efficiently explored

Buckyball Polymer Nanocomposites
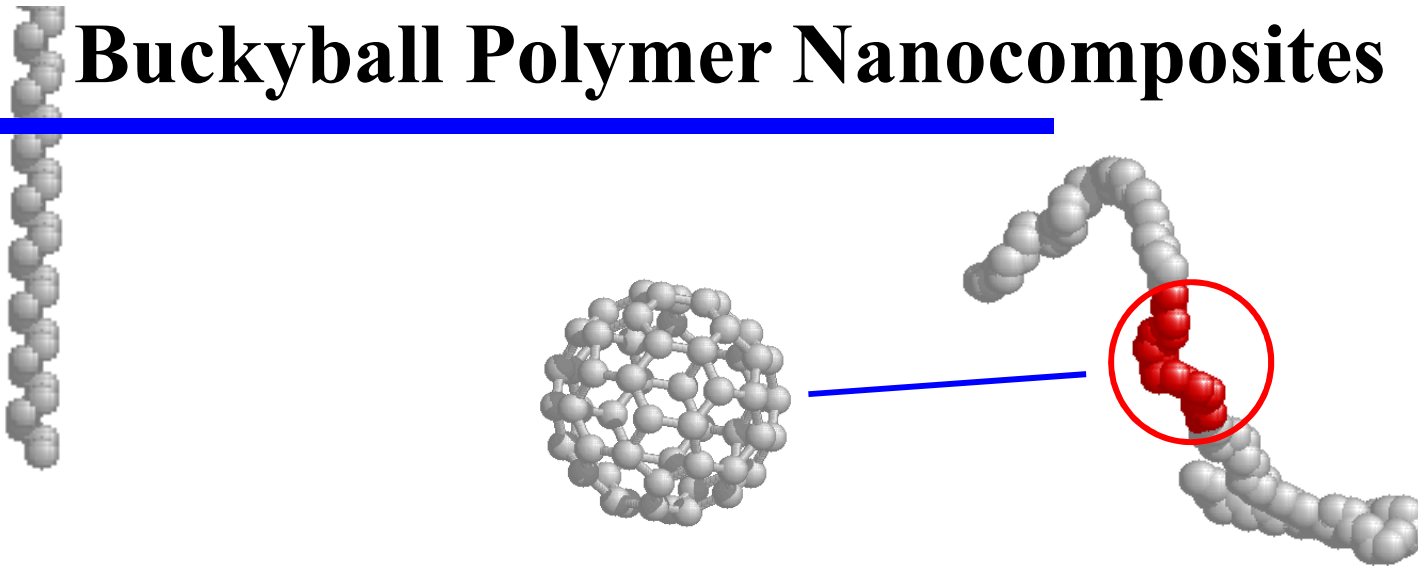
bead-ball distribution
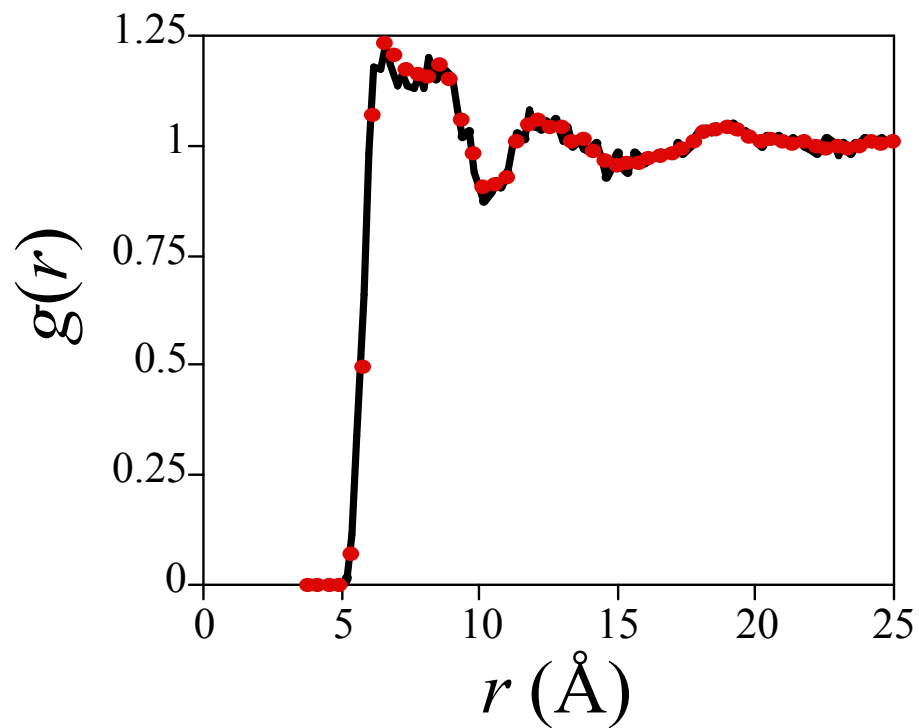
bead-ball interaction
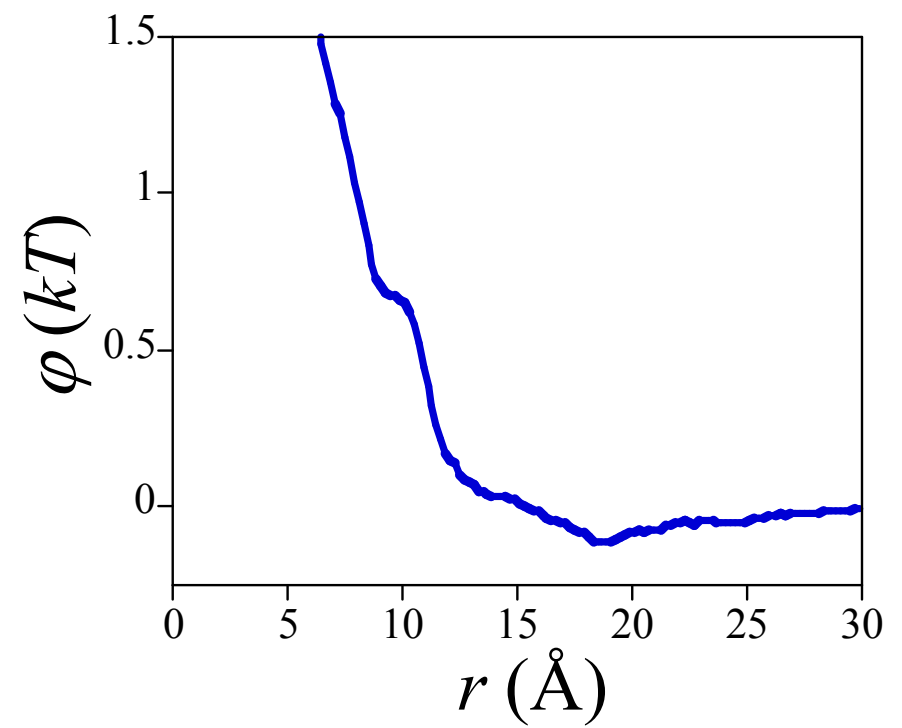
Conclusions

- 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?
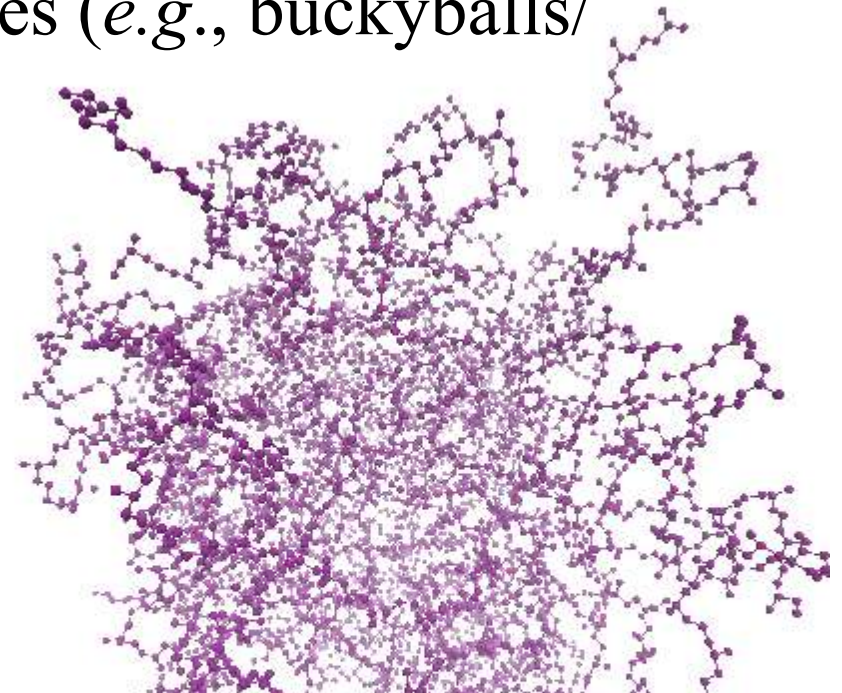
Lets stop and think about thermodynamics a bit here.

Modeling of Aqueous Poly(oxyethylene) Solutions. 2. Mesoscale Simulations

Jan Fischer,[†] Dietmar Paschek,[‡] Alfons Geiger,[‡] and Gabriele Sadowski*,[†]

Laboratory of Thermodynamics and Department of Physical Chemistry, Dortmund University of Technology, 44221 Dortmund, Germany

We extend our work on aqueous solutions of poly(oxyethylene) oligomers $H-(CH_2-O-CH_2)_n-H$ (POE_n). On the basis of atomistic simulations of trimer and decamer solutions (first part of this series of papers), different sets of coarse-grained implicit-solvent potentials have been constructed using the iterative Boltzmann inversion technique. The comparison of structures obtained from coarse-grained simulations (gyration radii, end-to-end distances, radial distribution functions) with atomistic reference simulations and experiments shows
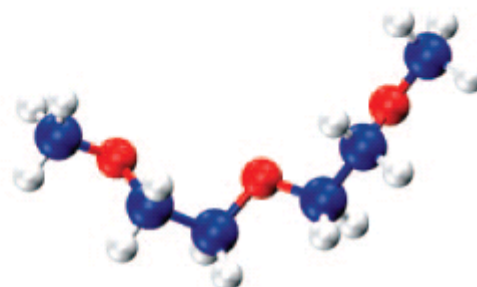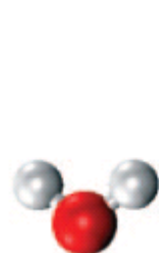
(a) H$_2$O   and   H-(CH$_2$-O-CH$_2$)$_3$-H

(b) (EO)$_3$

Figure 1. Applied mapping scheme for poly(oxyethylene) water solutions. The atomistic representation (a) is mapped onto its coarse-grained implicit-solvent counterpart (b) by assigning the mesoscale group "EO" to the center of mass of each [H$_2$C−O−CH$_2$] repeat unit ([H$_3$C−O−CH$_2$] unit at molecule ends).

evaluating the functions of interest. After each iteration loop, the potential(s) 1,..., n are corrected according to the formula

$$U_{i+1}^{j}(x) = U_{i}^{j}(x) + RT \ln \frac{P_i^j(x)}{P_{tgt}^j(x)} \qquad j = 1,..., n \quad (1)$$

$P_{tgt}^j(x)$ denotes the target distribution for the jth potential, $P_i^j(x)$ denotes the jth distribution function resulting after iteration loop i and from the use of the actual potential $U_i^j(x)$. $P^j(x)$ has to be

$$U_{\text{PMF,nb}}(r) = RT \ln g_{\text{tgt}}(r) \tag{2}$$

for nonbonded, bond-bending, bond-stretching, and dihedral

$$U_{\text{PMF,ang}}(\varphi) = RT \ln \frac{P_{\text{tgt}}(\varphi)}{\sin \varphi} \tag{3}$$

$$U_{\text{PMF,bd}}(r) = RT \ln P_{\text{tgt}}(r) \tag{4}$$

$$U_{\text{PMF,dihed}}(\varphi) = RT \ln P_{\text{tgt}}(\varphi) \tag{5}$$

Training the CG potential on trimer and decamer PEO
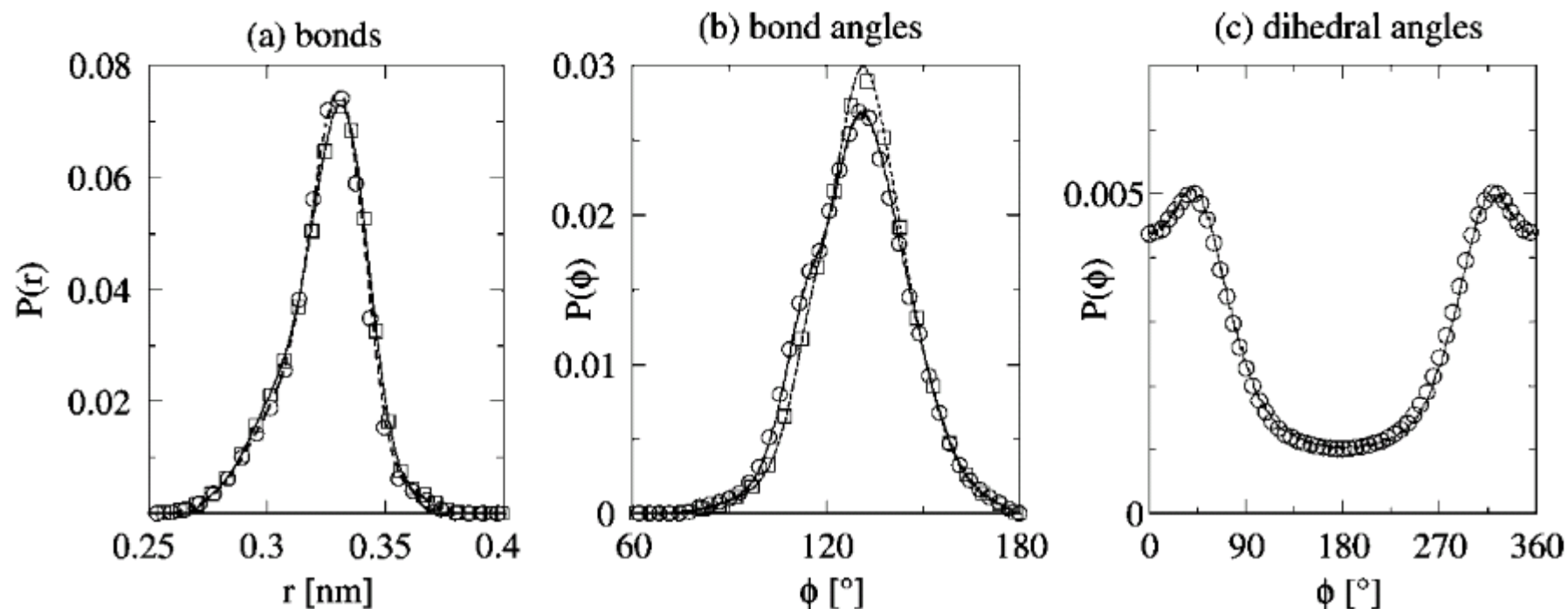
Figure 2. Histograms of intramolecular degrees of freedom between the monomers for the poly(ethyleneoxide) trimer and decamer in water at $w_{PEO} = 0.48$. The symbols denote the target distributions extracted from atomistic simulations using the modified TraPPE-UA force field:[21] the lines show the final trial distributions from Boltzmann iteration using coarse-grained molecular dynamics simulations. (a) Bond distance distribution between two neighboring EO sites (squares, trimer; circles, decamer). (b) Angle distribution between three joint EO sites (squares, trimer; circles, decamer) site. (c) Dihedral angle distribution between four joint EO sites (circles, decamer potential fit).
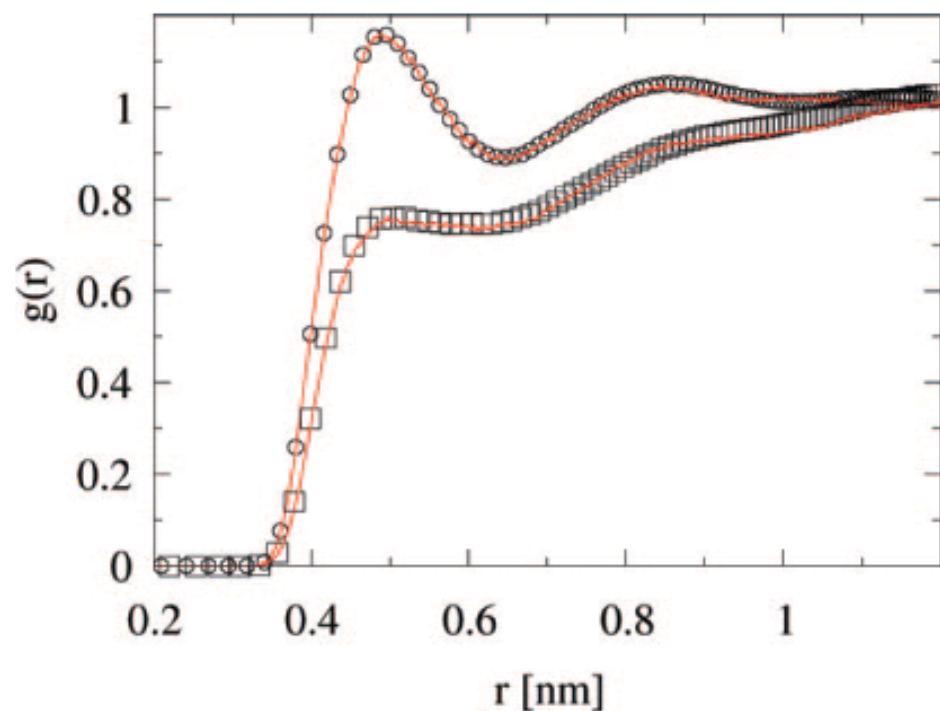
Figure 3. Intermolecular radial distribution functions between mesoscale ethylene oxide (EO) units in aqueous solution. The lines denote final radial distribution functions from Boltzmann iteration potential fits (lines for decamer fits with and without dihedrals are virtually indistinguishable). Circles correspond to the target function for POE_3 and squares to the target function for POE_{10}. Both at $w_{POE} = 0.48$ ($\rho_{POE} = 484$ kg/m^3). Both targets are from atomistic trajectories at 298 K and 1 bar. Mapping as depicted in Figure 1.

Figure 4. Final nonbonded potentials between mesoscale interaction sites "EO" from Boltzmann iteration (cutoff 1 nm). Full line, POE_3 fit; broken line, POE_{10} fit without dihedral potential; dotted line, POE_{10} fit using an additional dihedral potential. Both at $w_{POE3} = 0.48$ ($\rho_{POE} = 484$ kg/m^3). Mesoscale sites were mapped as described in Figure 1.
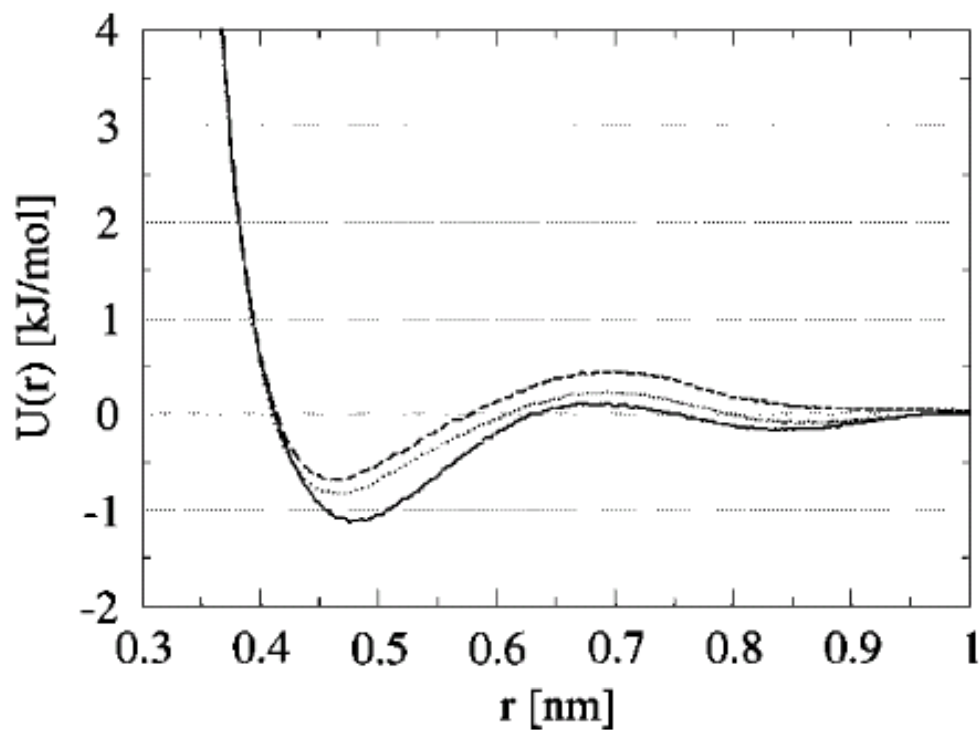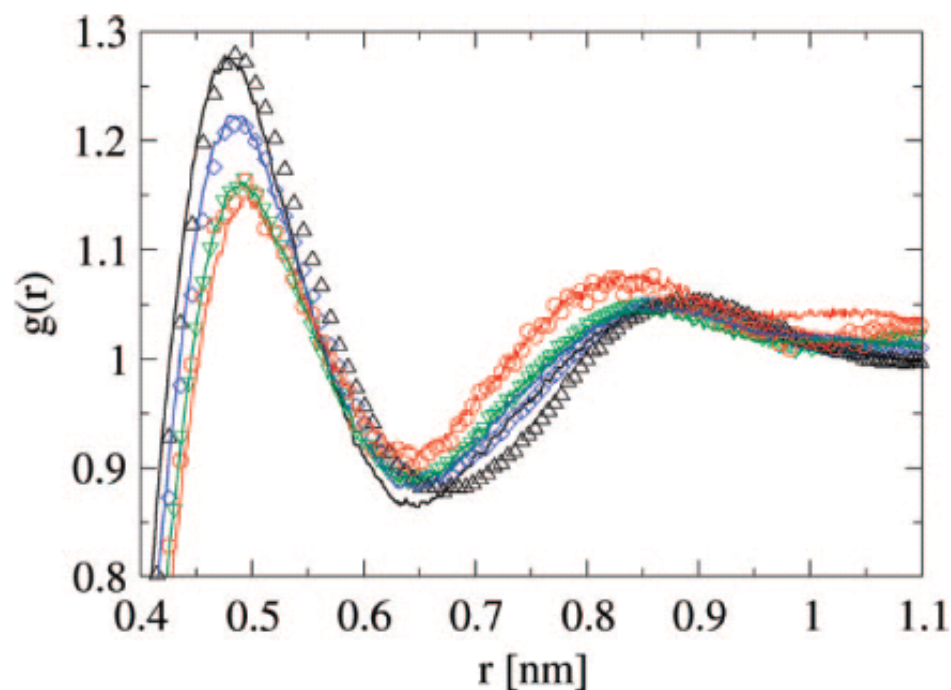
Figure 5. Radial distribution functions at different concentrations between EO sites from atomistic and coarse-grained simulations of POE$_3$ in water using the potentials (see Figure 4) adjusted to reproduce the structure at 298 K, 1 bar, and $w_{POE3} = 0.48$. Symbols denote results from atomistic simulations, and lines display results from mesoscale simulations. Concentrations: $w_{POE3} = 0.15$ (red)/0.48 (green)/0.66 (blue)/ 0.81 (black).
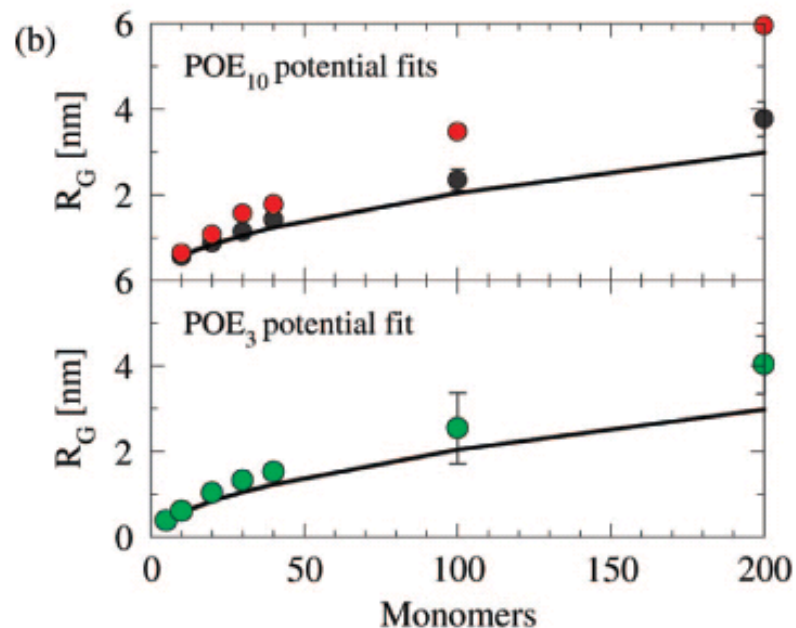
CG vs Detailed MD
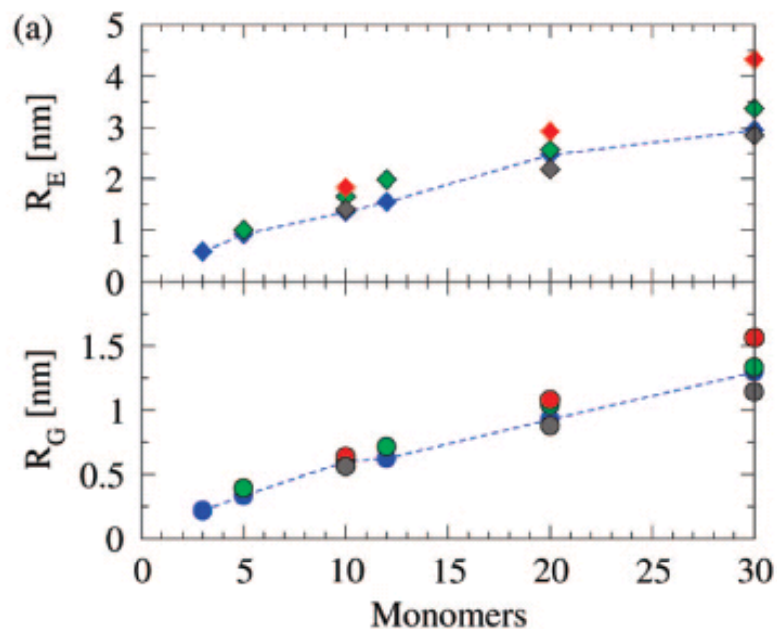
CG vs Experiment

Figure 10. Dependence of radius of gyration R_G (circles) and end-to-end distance R_E (diamonds) on chain length for poly(oxyethylene) in water at 298 K and 1 bar. (a) R_G and R_E from *atomistic simulations* (blue symbols with line) compared to coarse-grained simulations with implicit-solvent potentials, employing trimer-fitted potentials (green symbols) and decamer-fitted potentials without dihedral interactions (red symbols) and decamer-fitted potentials including dihedral interactions (gray symbols). (b) R_G from coarse-grained simulations compared to values calculated by extrapolation of experimental data[32] (line). The key to the symbols is the same as in part a. All simulations and potential fits at a POE mass density of $\rho_{POE} = 484$ kg/m^3, except for 100-mer and 200-mer simulations (240 kg/m^3). Each monomer consists of one repeat unit CH_2-O-CH_2.

Concentration dependence
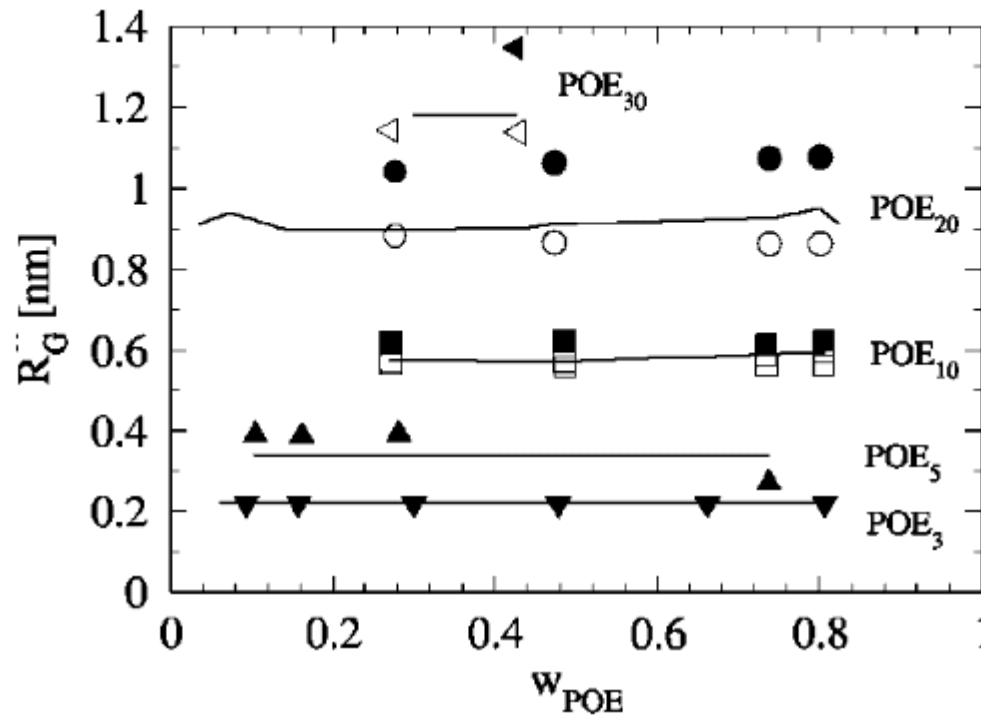
Figure 11. Concentration dependency of radius of gyration of POE_n with $n = 3, 5, 10, 12, 20,$ and 30 repeat units. Atomistic simulations (lines) compared to simulations with trimer-fitted potentials (full symbols) and simulations with decamer-fitted potentials including dihedral interactions (open symbols).
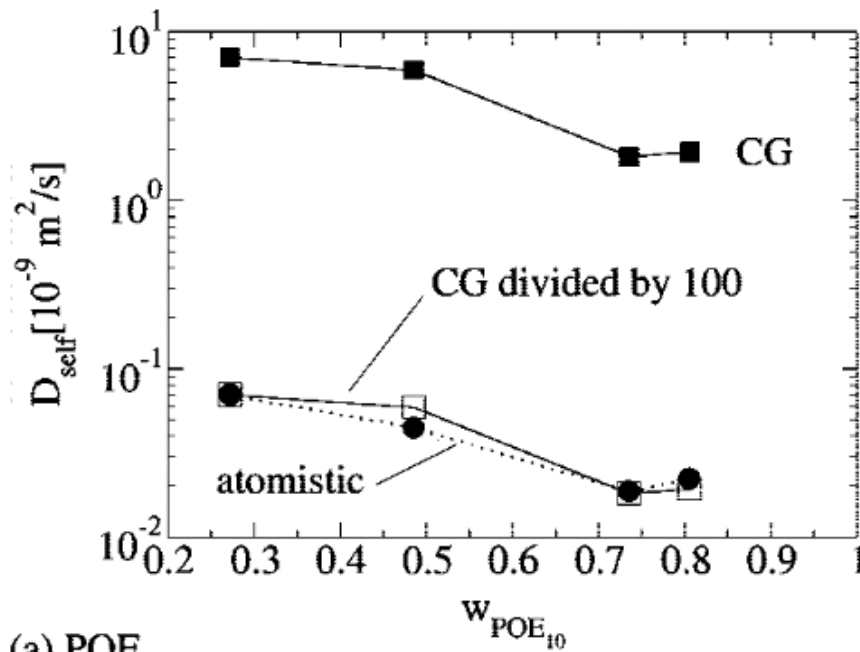
(a) POE$_{10}$
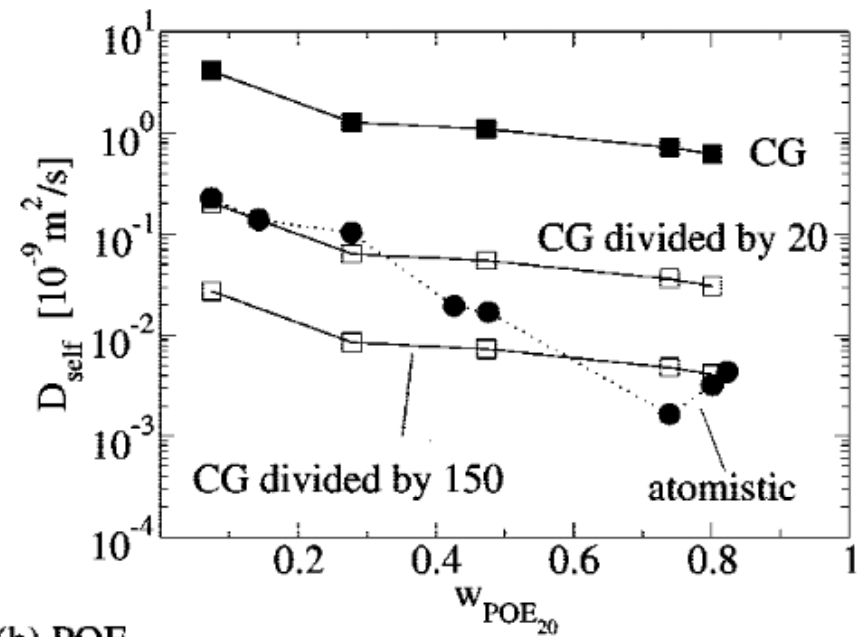
(b) POE$_{20}$

If carefully devised for **your system of interest**, CG potentials can be quite useful for estimating properties of larger systems, or more concentrated systems, etc.
(Speed up by a factor of 10 to 100).

Simulation of polymer melts. I. Coarse-graining procedure for polycarbonates

W. Tschöp[+#], K. Kremer[++], J. Batoulis[+++], T. Bürger[+++] and O. Hahn[++]*

[+]   IFF, Forschungszentrum Jülich, Postfach 19 13, D-52425 Jülich, FRG
[++]   Max-Planck-Institut für Polymerforschung, D-55021 Mainz, FRG
[+++] MD-IM-FA, Bayer AG, D-51368 Leverkusen, FRG
[#]   Now at Xerox Palo Alto Research Center, 3333 Coyote Hill Road, Palo Alto, CA 94304, USA

The paper introduces a systematic procedure to coarse grain atomistic polymer models into a mesoscopic model, which then allows an effective and fast simulation of melts. The method, which provides information on both static and dynamic properties, is tested for three different modifications of polycarbonate. The models successfully describe the variation in the Vogel–Fulcher temperature as well as the total chain extension. The effective speedup compared to the corresponding atomistic simulation is significantly above 10^3.
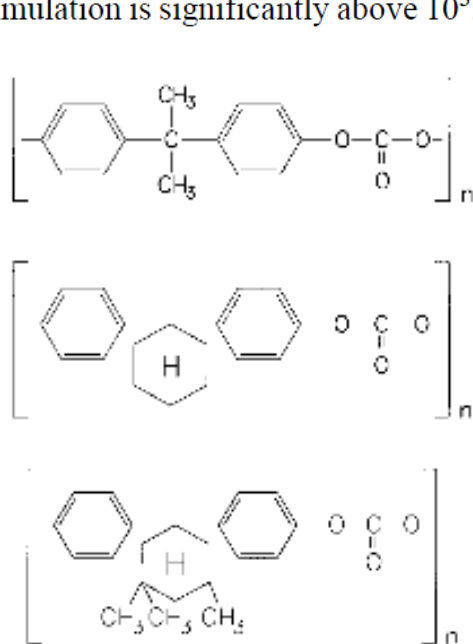
Fig. 2. Structures of the three different polycarbonates investigated with the present coarse-graining simulation approach.
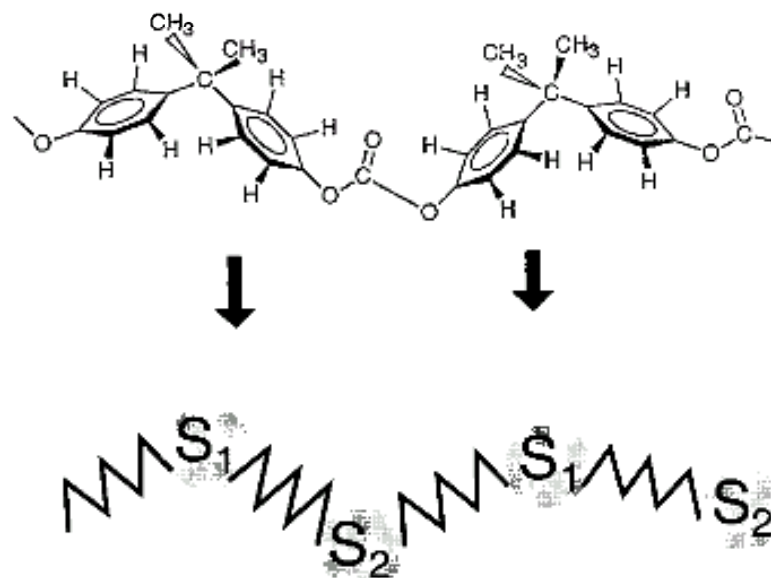

Fig. 3. Illustration of the 1:2 mapping of BPA-PC. The center of the sphere S_1 is given by the geometrical center of the isopropylidene group (CH_3-C-CH_3), while S_2 corresponds to the geometrical center of the carbonate group.

What about water?

- Pure water: phase behavior, anomalies.

- Hydrophobic solvation and interactions

- Ionic solvation

- Self-assembly

What about water?

- Modeling of water in simulations

- Quantum and classical models

- Can we coarse-grain water?

    -- pure water

    -- solvation phenomena

Can we coarse-grain water?
See papers by

- T. Head Gordon and Stillinger, JCP 1993.

- Garde and Ashbaugh, JCP, 2001

- Greg Voth's papers on water.

- Johnson et al. (see next page).

Representability problems for coarse-grained water potentials

Margaret E. Johnson
UCSF/UCB Joint Graduate Group in Bioengineering, University of California, Berkeley, California 94720

Teresa Head-Gordon[a]
UCSF/UCB Joint Graduate Group in Bioengineering, University of California, Berkeley, California 94720 and Department of Bioengineering, University of California, Berkeley, California 94720

Ard A. Louis[a]
Department of Chemistry, University of Cambridge, Lensfield Road, Cambridge CB2 1EW, United Kingdom

Questions?