SAND2017-4586C

Going up in Time and Length Scales in Modeling Polymers

Gary S. Grest

Center for Integrated Nanotechnologies
Sandia National Laboratories
Albuquerque, NM

Les Houches, May 16, 2017

Sandia National Laboratories is a multi-program laboratory managed and operated by Sandia Corporation, a wholly owned subsidiary of Lockheed Martin Corporation, for the U.S. Department of Energy's National Nuclear Security Administration under contract DE-AC04-94AL85000.

Computational Challenges in Polymers

- Longest relaxation time $\tau \sim N^3$

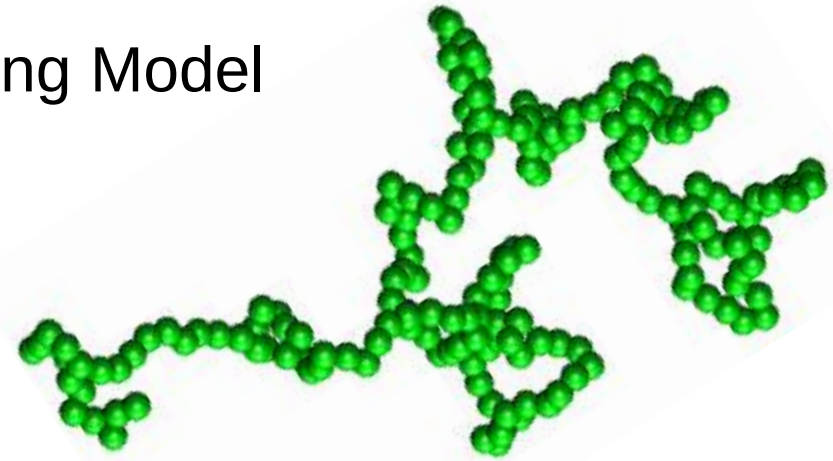
- Chains are Gaussian coils – $R \sim N^{1/2}$
  - Number of chains must increase as $R^3 \sim N^{3/2}$ so polymer chains do not to see themselves through periodic boundary conditions

- Double chain length – cpu required increases by at least a factor of $2^{4.5} \sim 23$
  - 1-2 month simulation becomes 2-4 years

- Number of processors limited: ~ 500-1000 particles/processor

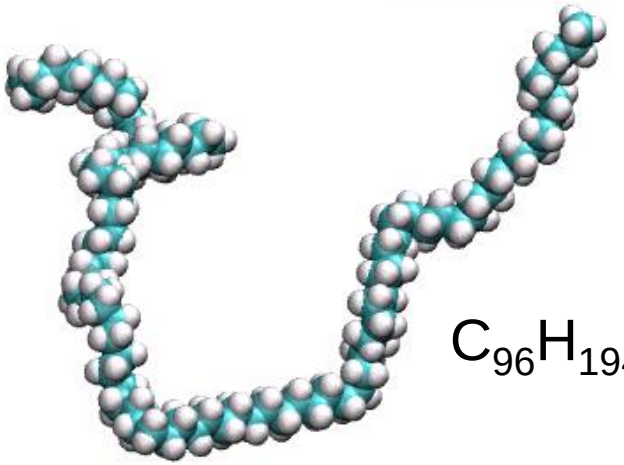
Polymer Simulation Models

- Bead-Spring Model



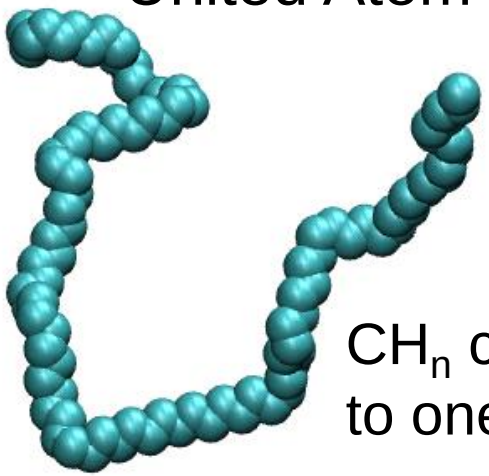
N=200

- Atomistic: All Atom



$C_{96}H_{194}$

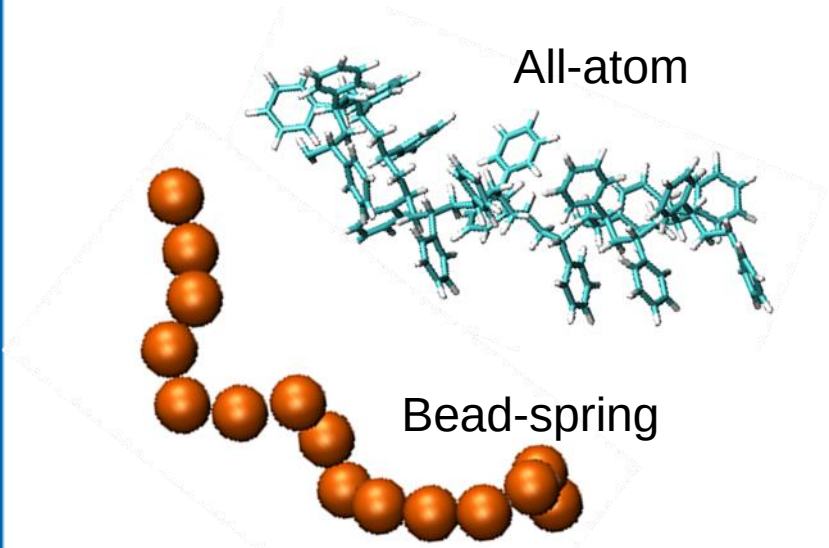
United Atom



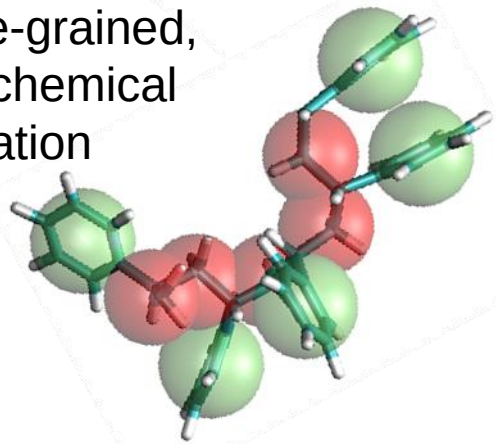
CH_n combined to one bead

Coarse-Graining of Polymers

- To reach larger length/time scales, new coarse graining methods are an active area of research



Coarse-grained, retain chemical information

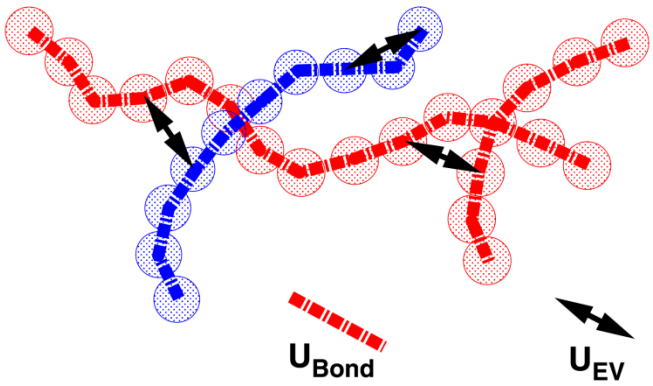


- Reduced number of degrees of freedom, simpler interaction potentials, reducing the overall computational effort
- Larger time steps (10-20x)
- Reduced effective bead friction due to lower energy barriers and/or a smoother energy landscape
- Back-mapping to fully atomistic model

Bead-Spring Model

- Short range - excluded volume interaction

$$U_{LJ}(r) = \begin{cases} 4\epsilon\left\{(\sigma/r)^{12} - (\sigma/r)^{6} + \frac{1}{4}\right\} & r \le r_c \\ 0 & r \ge r_c \end{cases}$$



- Bonded interaction - FENE spring

$$U_{FENE}(r) = \begin{cases} -0.5kR_o^2 \ln\left(1 - (r/R_o)^2\right) & r \le R_o \\ \infty & r > R_o \end{cases}$$

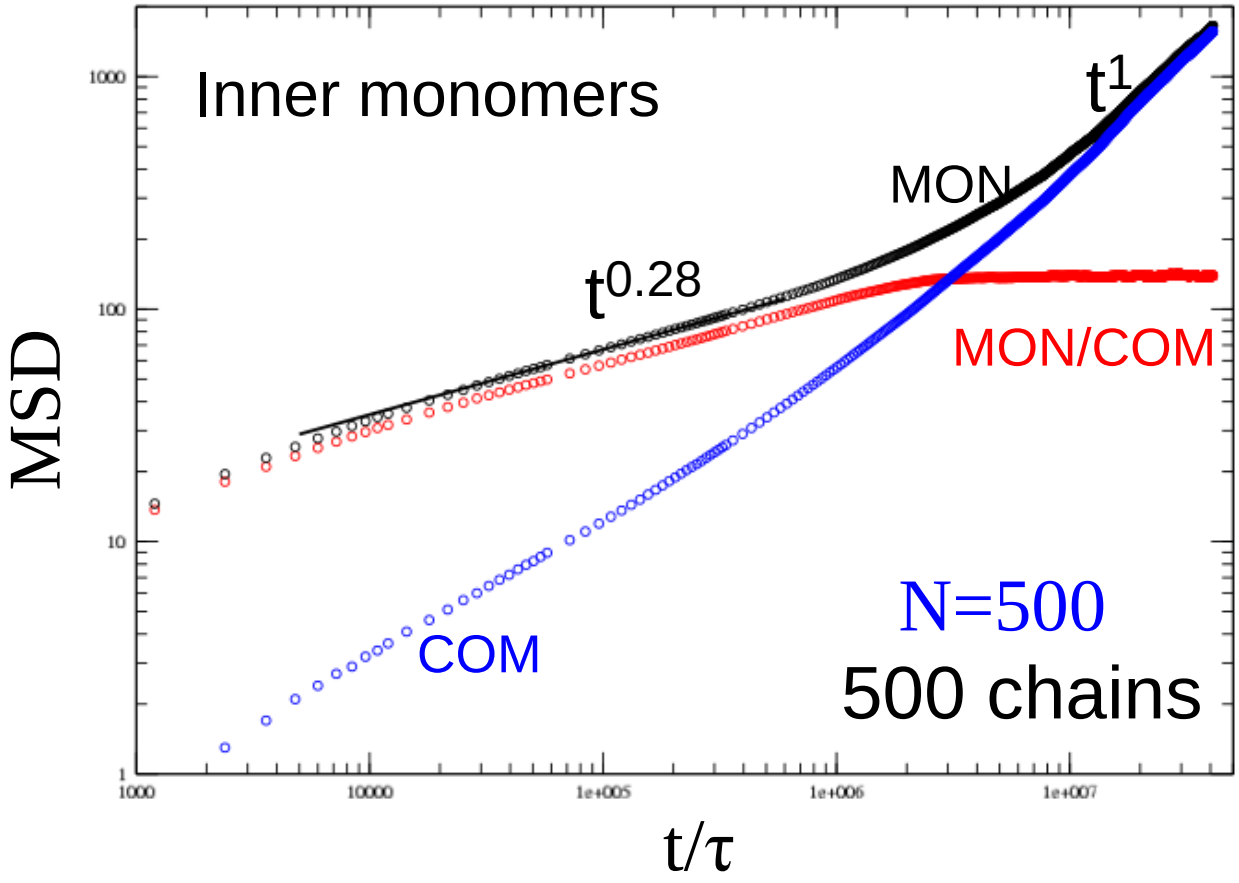
$k=30\varepsilon/\sigma^2$, $R_o=1.5\sigma$

- Energy barrier prohibits chains from cutting through each other topology conserved

$$m_i \frac{d^2\vec{r}_i}{dt^2} = -\vec{\nabla} \cdot U_i - m_i \Gamma \frac{d\vec{r}_i}{dt} + \vec{W}_i(t)$$

Time step $\Delta t \sim 0.01\tau$, $\tau=\sigma(m/\varepsilon)^{1/2}$

State of the Art: Motion of Entangled Polymer

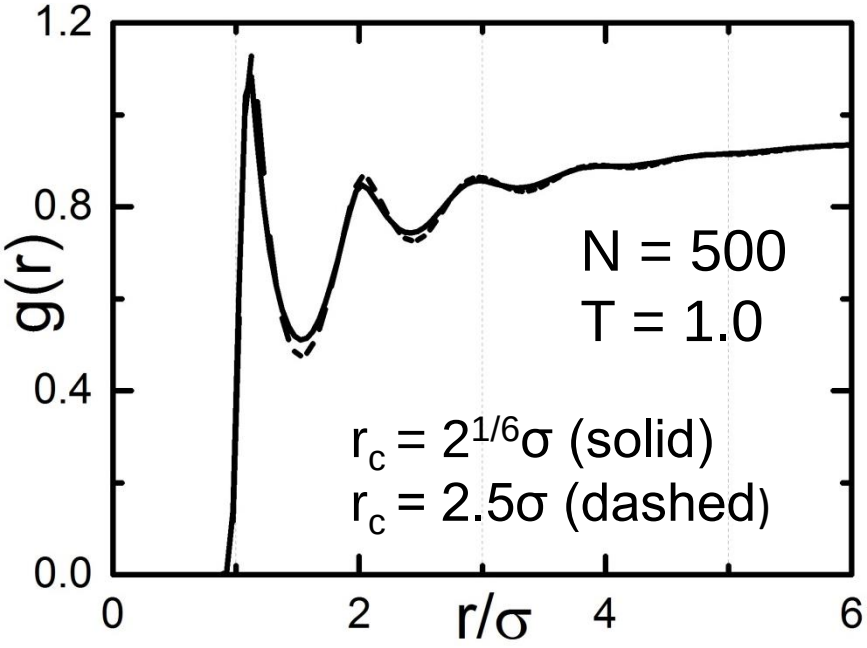


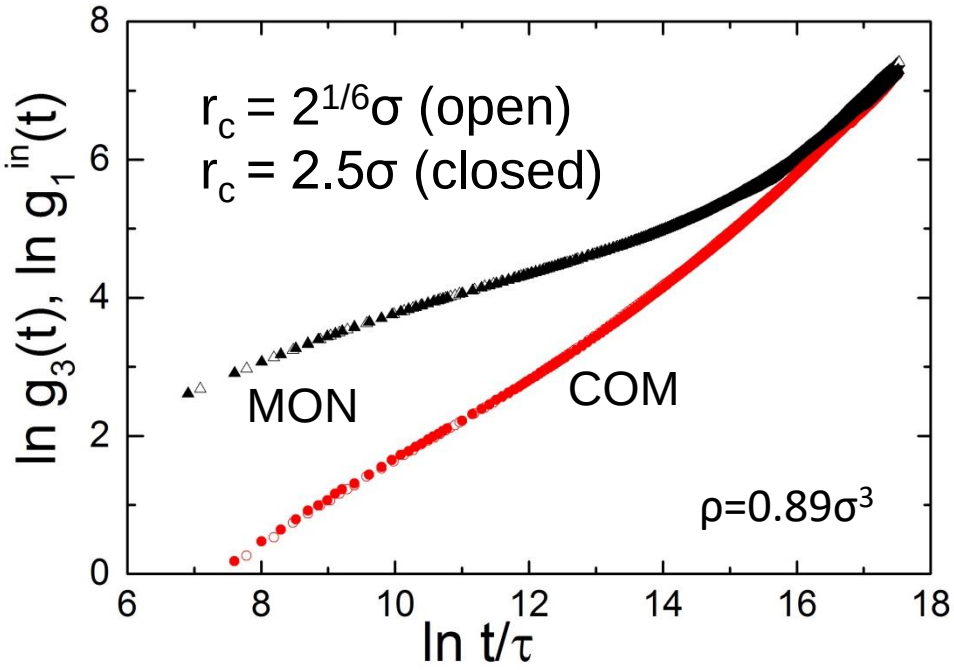
2 million core hours

- $t^{1/4}$ motion is clearly seen for inner monomers
- Theoretically predicated second $t^{1/2}$ region still unresolved

Effect of Attractive Interactions

- Purely repulsive interactions widely used for modeling melts
  - computationally the most efficient





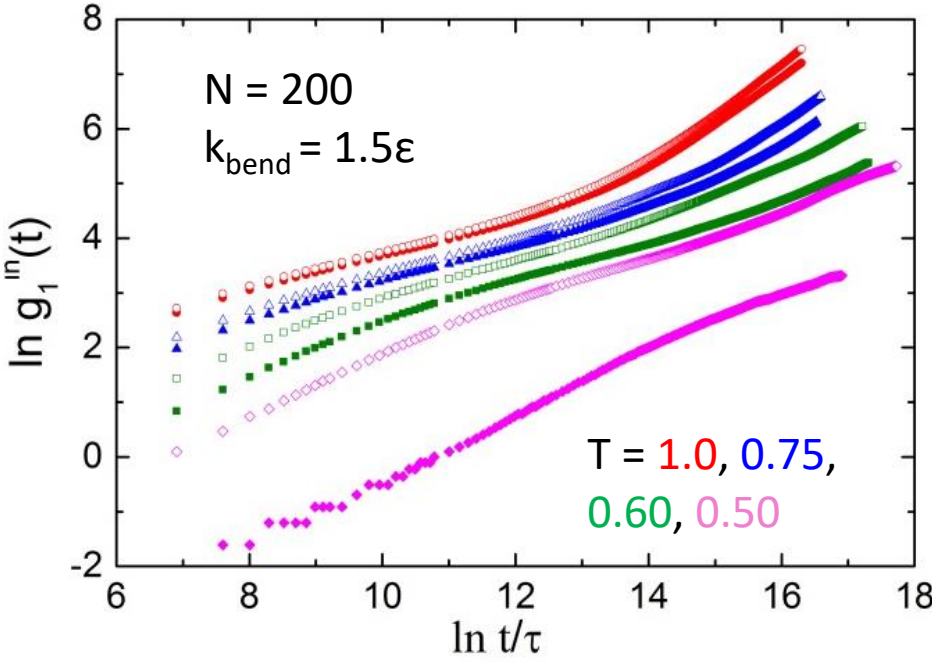
- Attractive interactions have essentially no affect on melt properties
- Justify implicit assumption that the dynamics of entangled polymers melts can be studied with short range, repulsive interactions

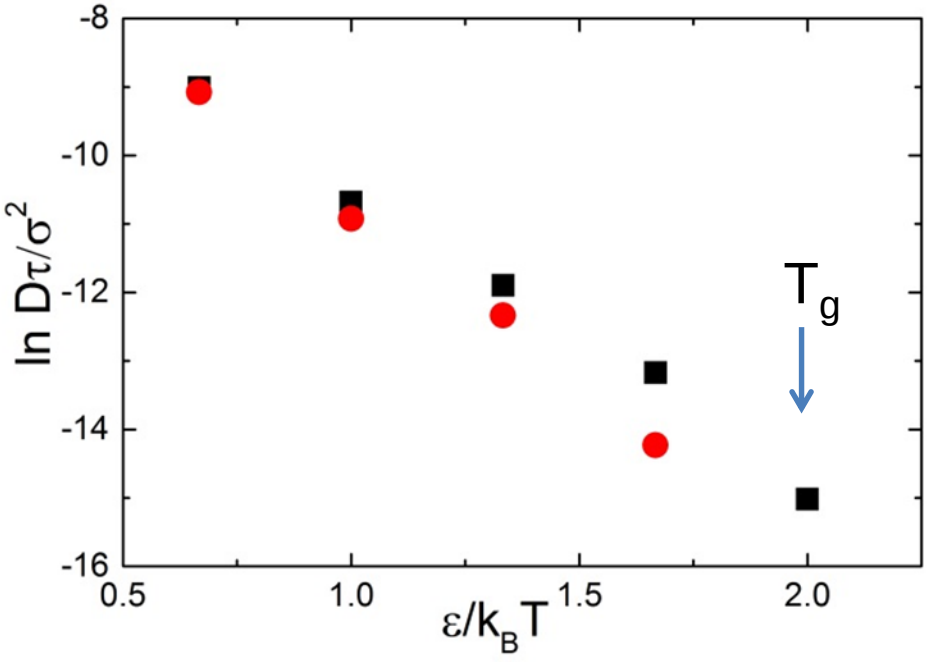
Grest. JCP (2016), in press

Attractive Interactions: Temperature Effects

- Cool melt slowly at constant pressure
- Compare repulsive and attractive interactions

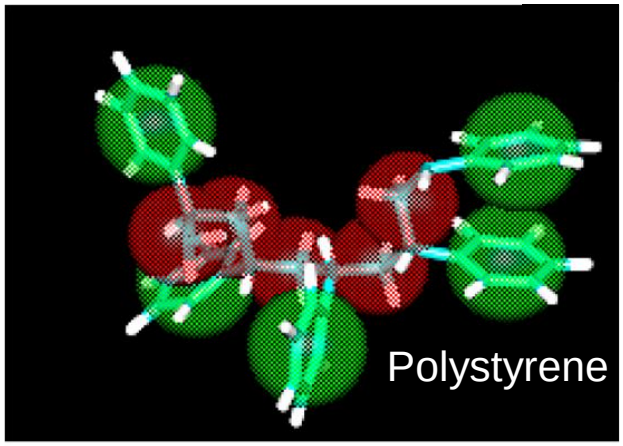
- Attractive interactions have little effect on the local packing, single chain statics and entanglement length N_e for all T

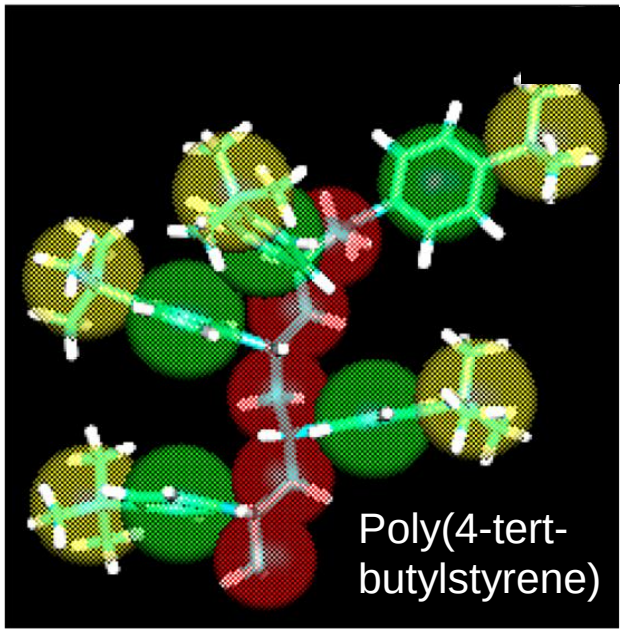




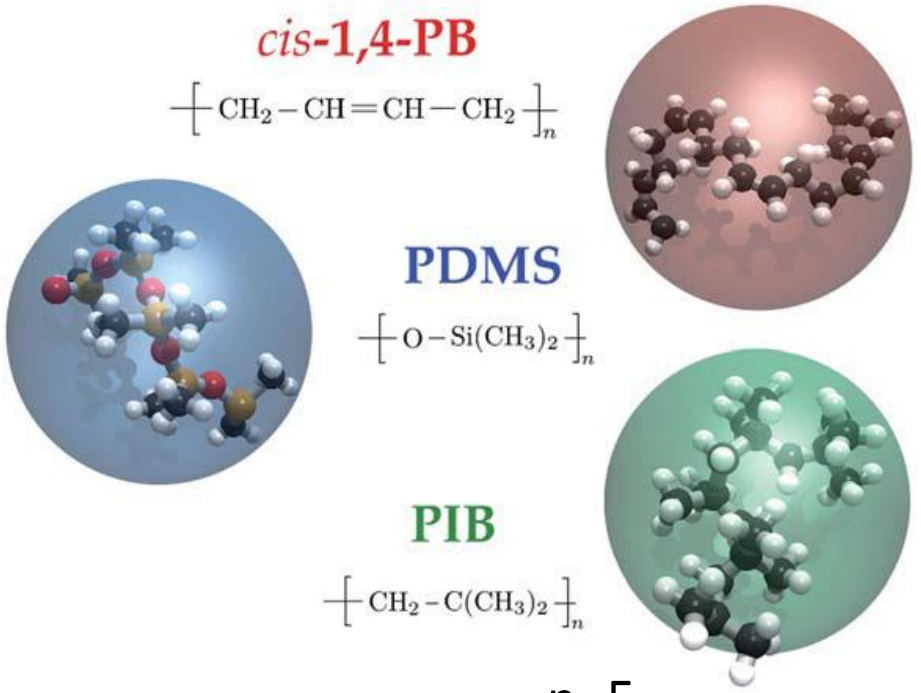
- Attractive interactions reduce chain mobility for $T < 2T_g$

Coarse Graining Polymers



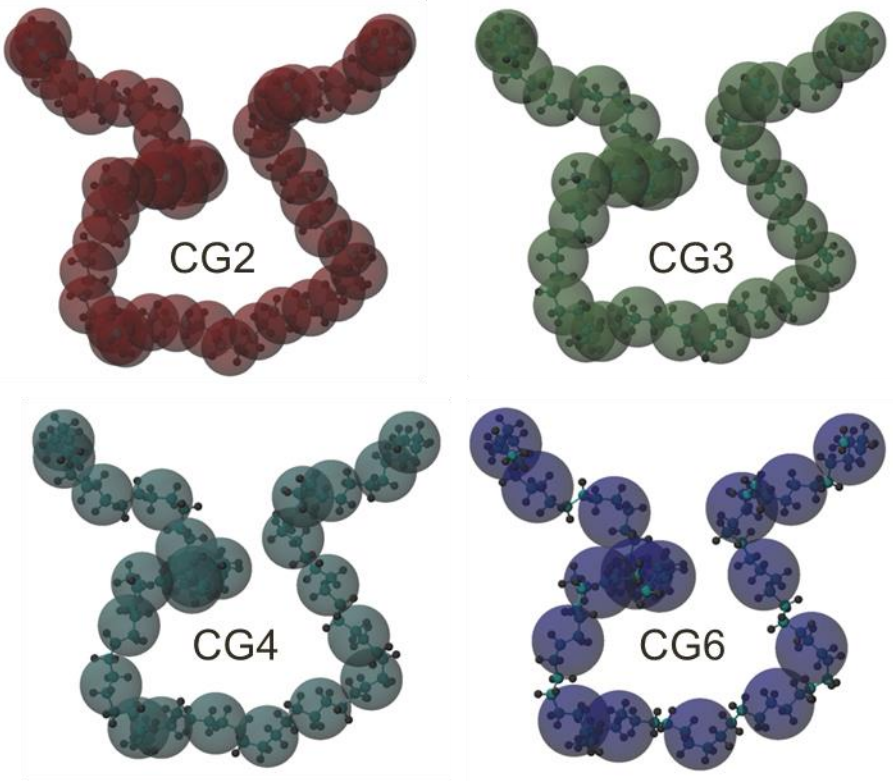


D. Fritz et al, Phys. Chem. Chem. Phys. 13, 10412 (2011);
A. Agrawal et al, Macromolecules 47, 3210 (2014)



G. Mauerl et al, RSC Adv., 5, 14065 (2015)

Degree of Coarse Graining Polyethylene



$C_{96}H_{194}$ chain with increasing degree of coarse graining

- Largest lengths scales of polymer dynamics are controlled by entanglements
- Shortest time and length scales required to resolve dynamic properties not obvious

- Probe the degree of coarse graining (CGing) required to simultaneously retain significant atomistic detail and access large length and time scales

K M Salerno et al, Phys Rev Lett 116, 058303 (2016)

Coarse-Graining Methodology

All-atom Melt MD simulation – LAMMPS*

↓

Define Beads

↓

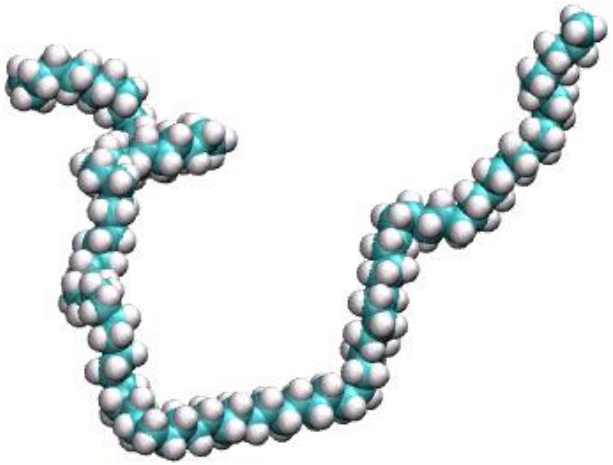
Bonded Interactions by Boltzmann Inversion

↓

Nonbonded Interactions by Iterative Boltzmann Inversion (IBI)

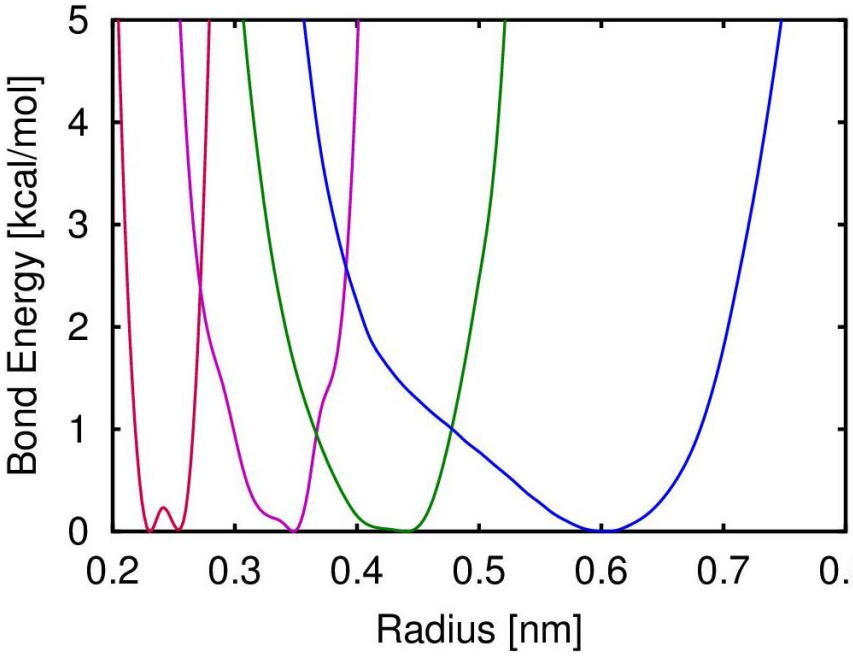
↓

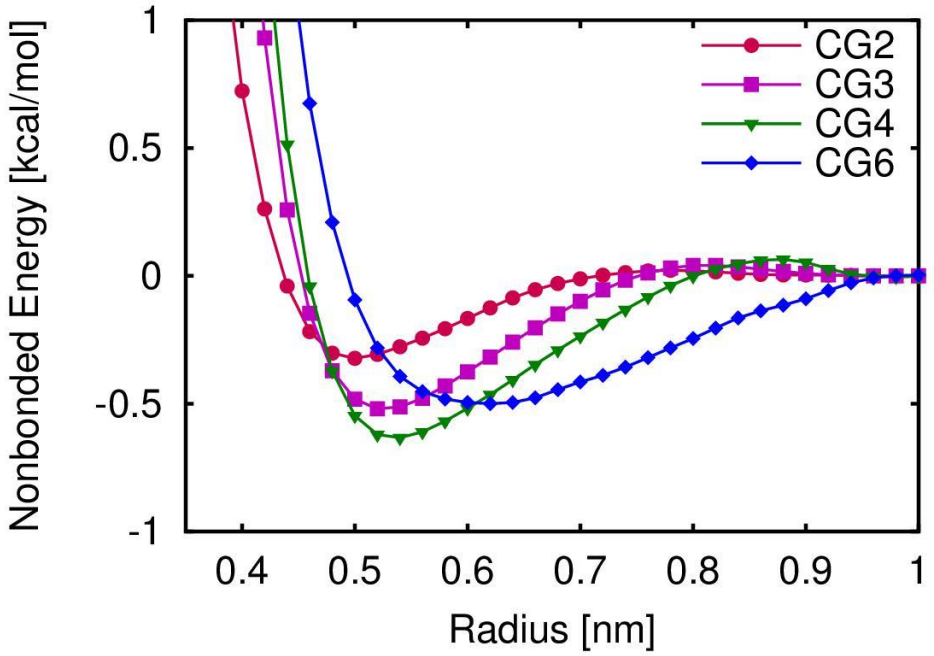
Validation



*http://lammps.sandia.gov/

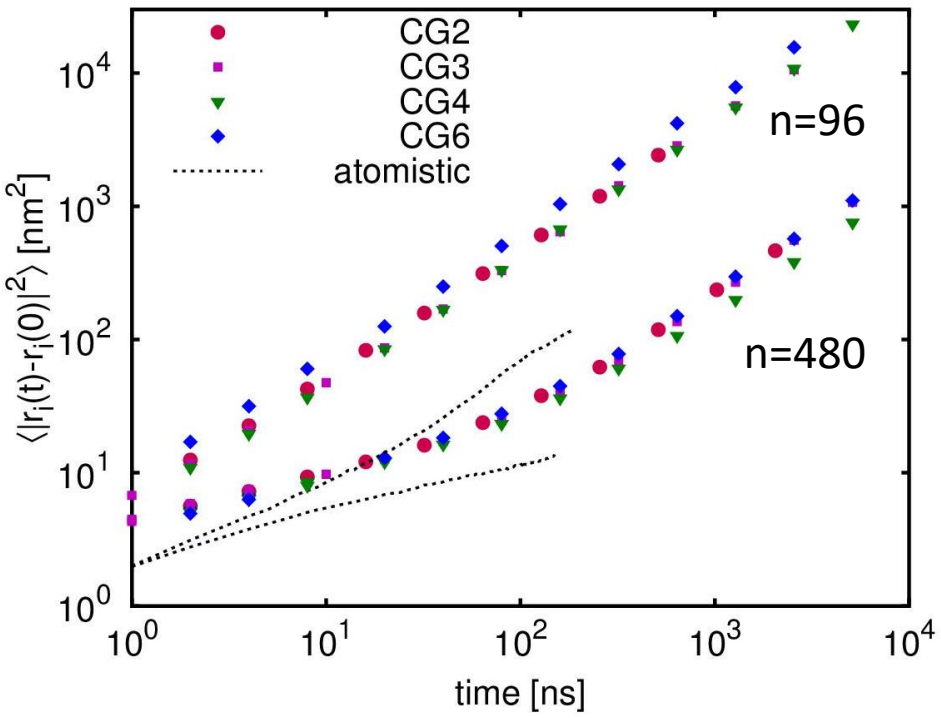
Coarse-Grained Potentials

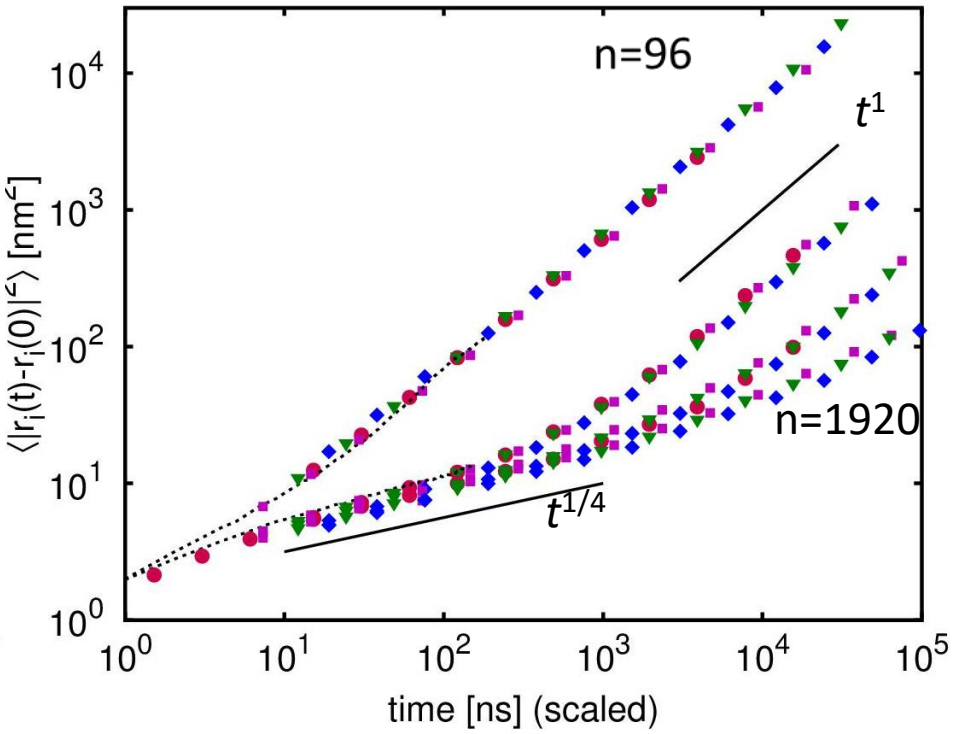




- Average bond length increases, bond distribution broadens as level of CGing increases
- Non-bonded potential softens as level of CGing increases
- Time step increases from 1 fs to 10 -20 fs for $\lambda \geq 3$
- ,Chains cut through each other for $\lambda = 6$
  - extra non-crossing constraint

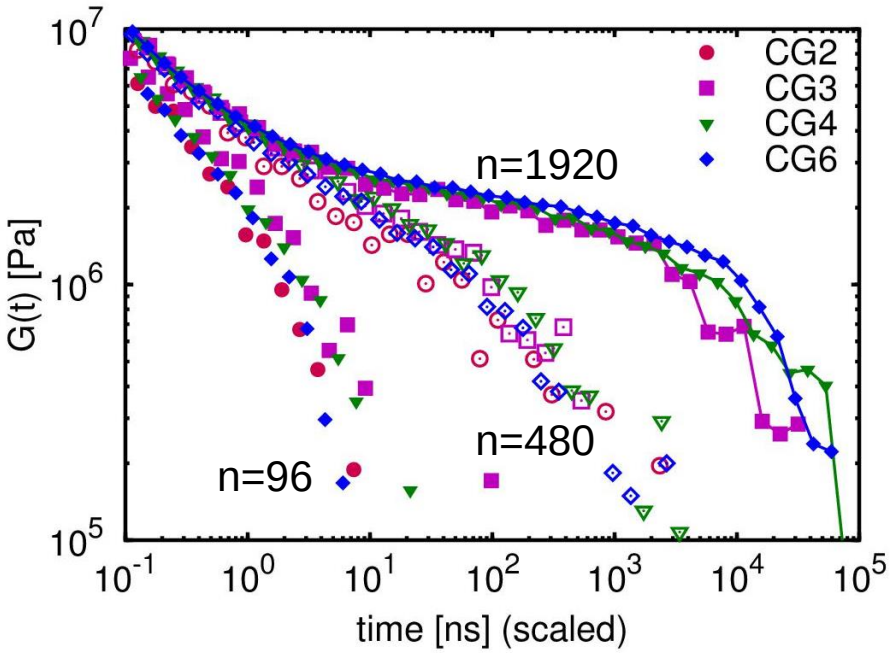
Chain Mobility

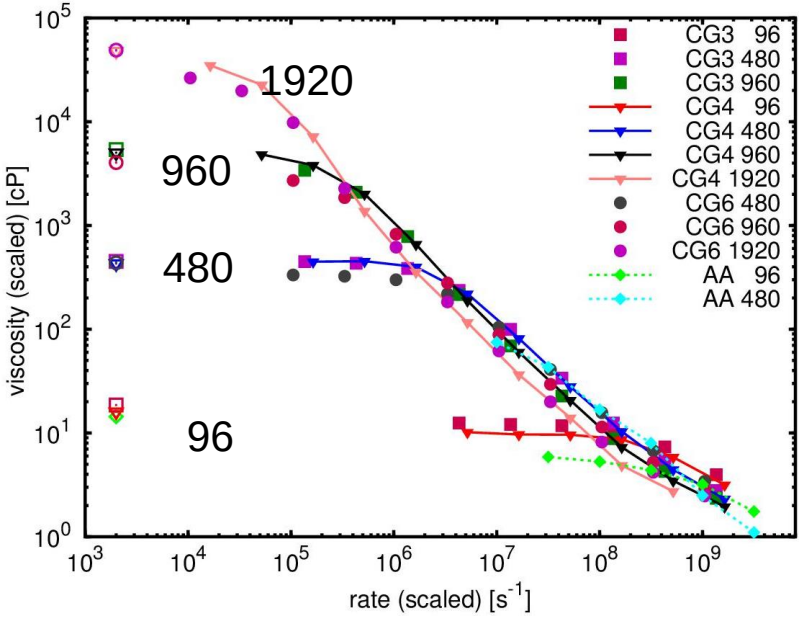




- Coarse graining reduces the number of degrees of freedom, creating a smoother free-energy landscape
- Dynamics of Coarse Grained models 6-10 times faster
- Consistent scaling factor for n = 96 – 1920

Stress Relaxation and Viscosity





- Longer, more entangled chains form progressively more distinct plateau region
  - Plateau modulus in good agreement with experiment
- Viscosity versus shear rate show shear thinning at high shear rates, crossing over to shear independent regime
- Time and length scales not accessible by atomistic models

Summary/Outlook

- Atomistic Simulations ideally suited for phenomena on local scale
  - Present limitations 100's nanoseconds, 10's nanometers

- Bead-spring models ideally suited for addressing general polymer phenomena, testing basic theoretical models
  - Disregards atomistic details
  - Can not quantitatively describe properties like structure, local dynamics

- Systematic coarse grained models can bridge the gap of time and length scales while retaining atomistic characteristics
  - Reduces number of degrees of freedom and increases fundamental time step
  - Captures the atomistic detail needed for correct dynamics from monomer to polymer scale

Acknowledgements

Collaborators:

- K. Michael Salerno, Brandon Peters (Sandia)
- Anupriya Agrawal (Washington University, St Louis)
- Dvora Perahia (Clemson)

Funding:

- Center for Integrated Nanotechnologies (CINT)
- DOE DE-SC007908