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Going up in time and length scales in modeling entangled polymers

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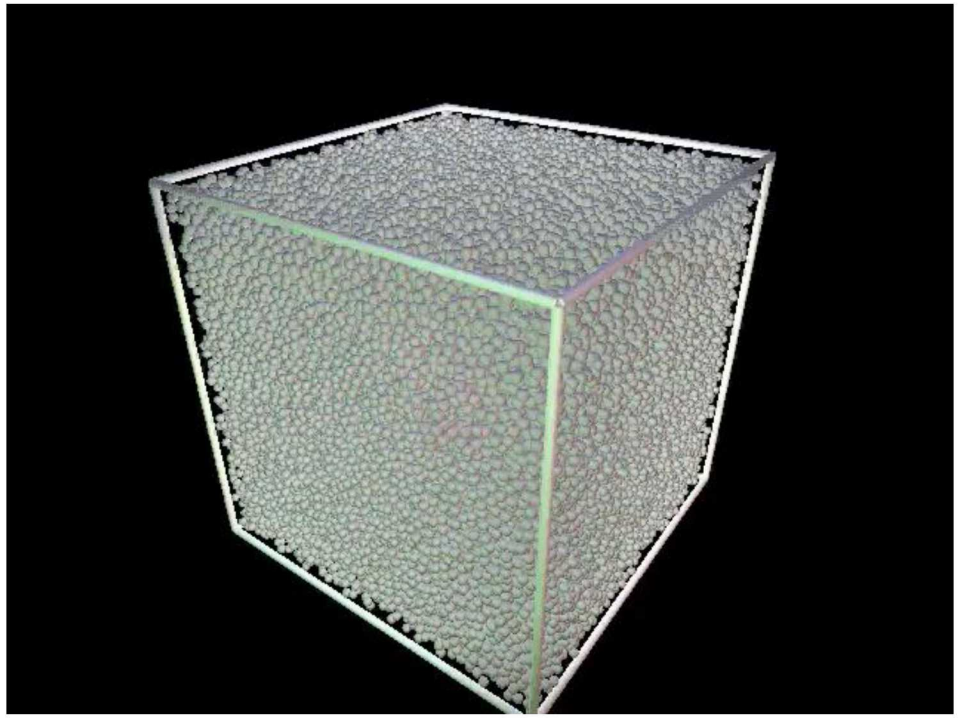
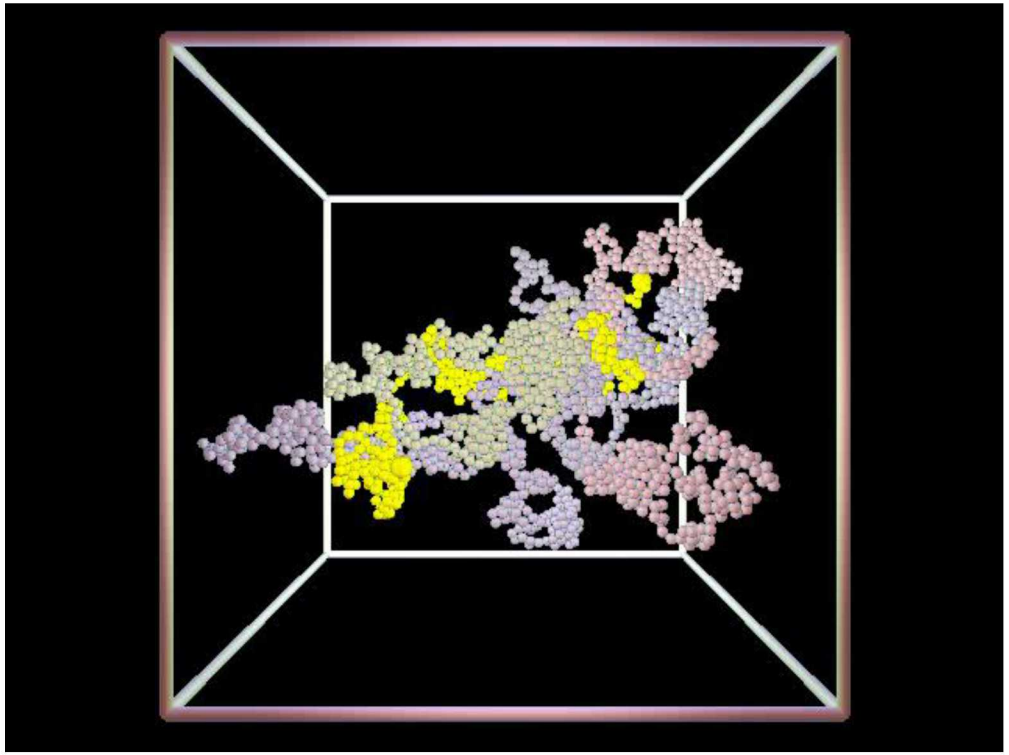
Polymer Motion

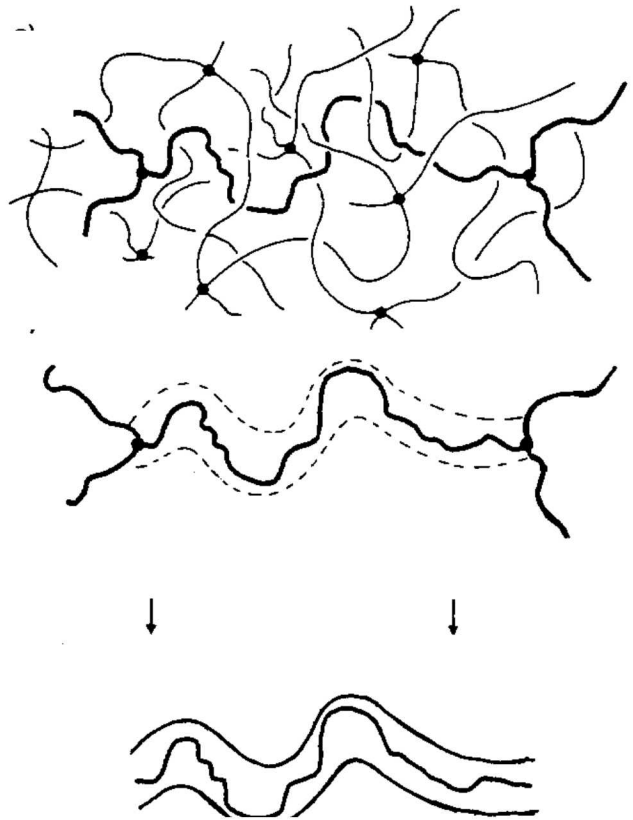
- Polymers are simultaneously hard and soft
  - –Unique Viscoelastic Behavior



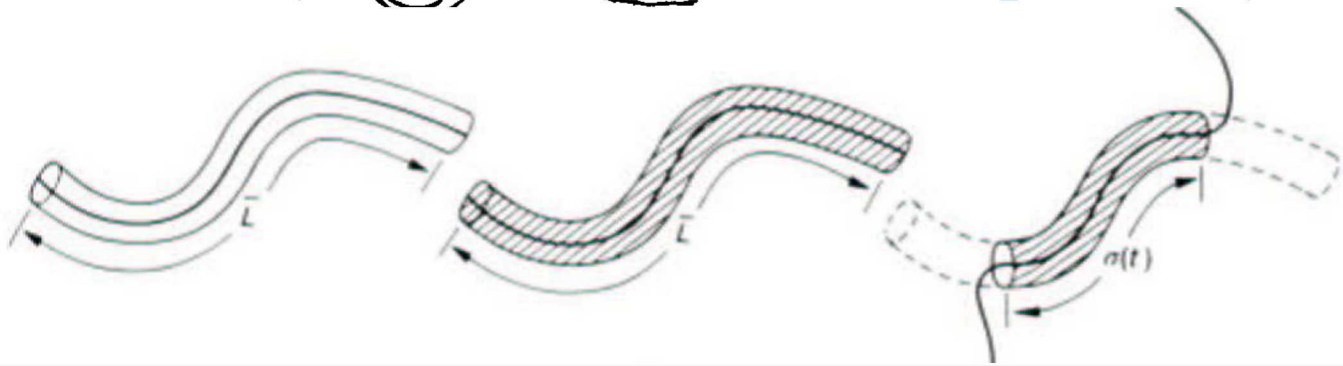


- Motion of a polymer chain is subject to topological constraints

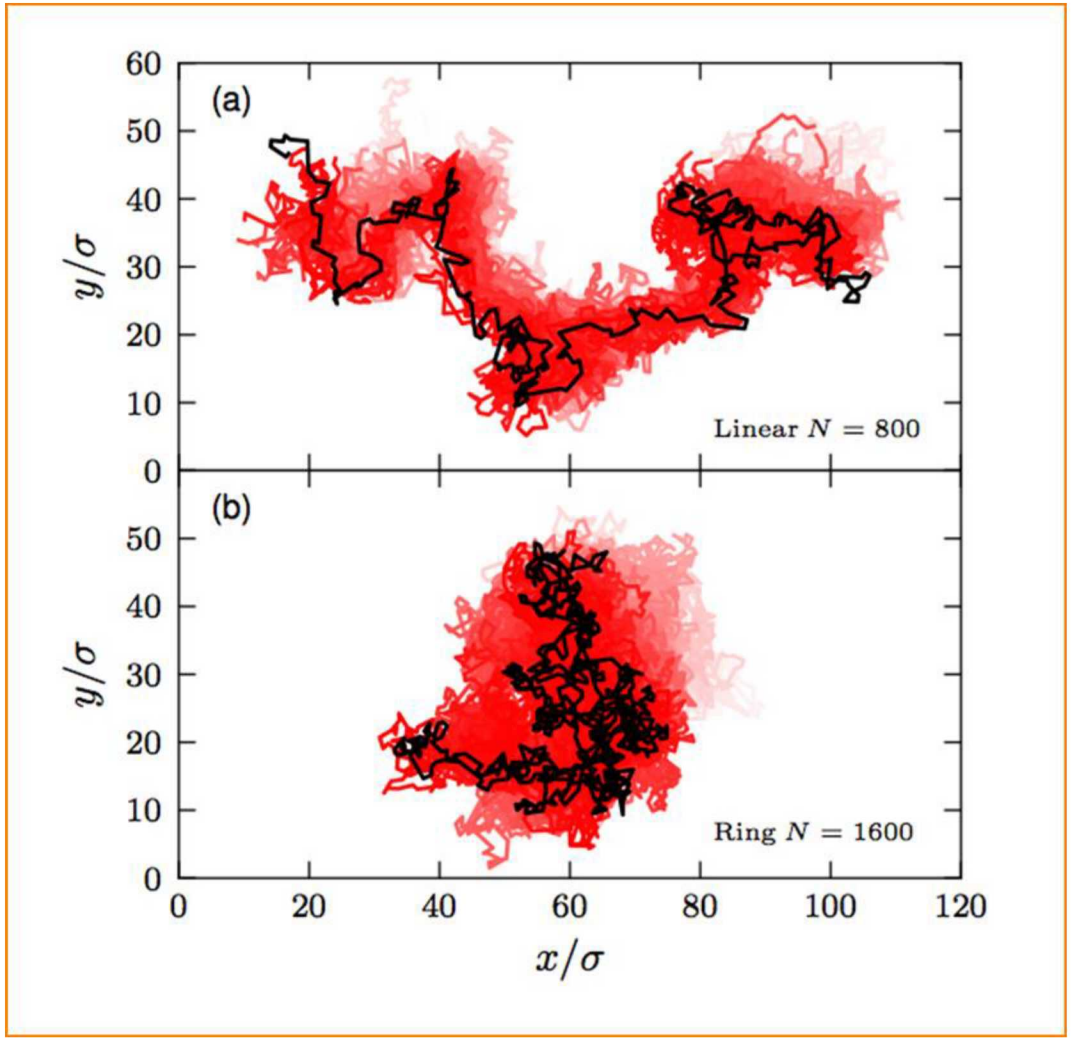
Polymer Motion in a Liquid



- Statistical Mechanics Approach
- Tube model (Edwards 1967)
- Reptation (de Gennes, 1971)



Polymer Topology Matters

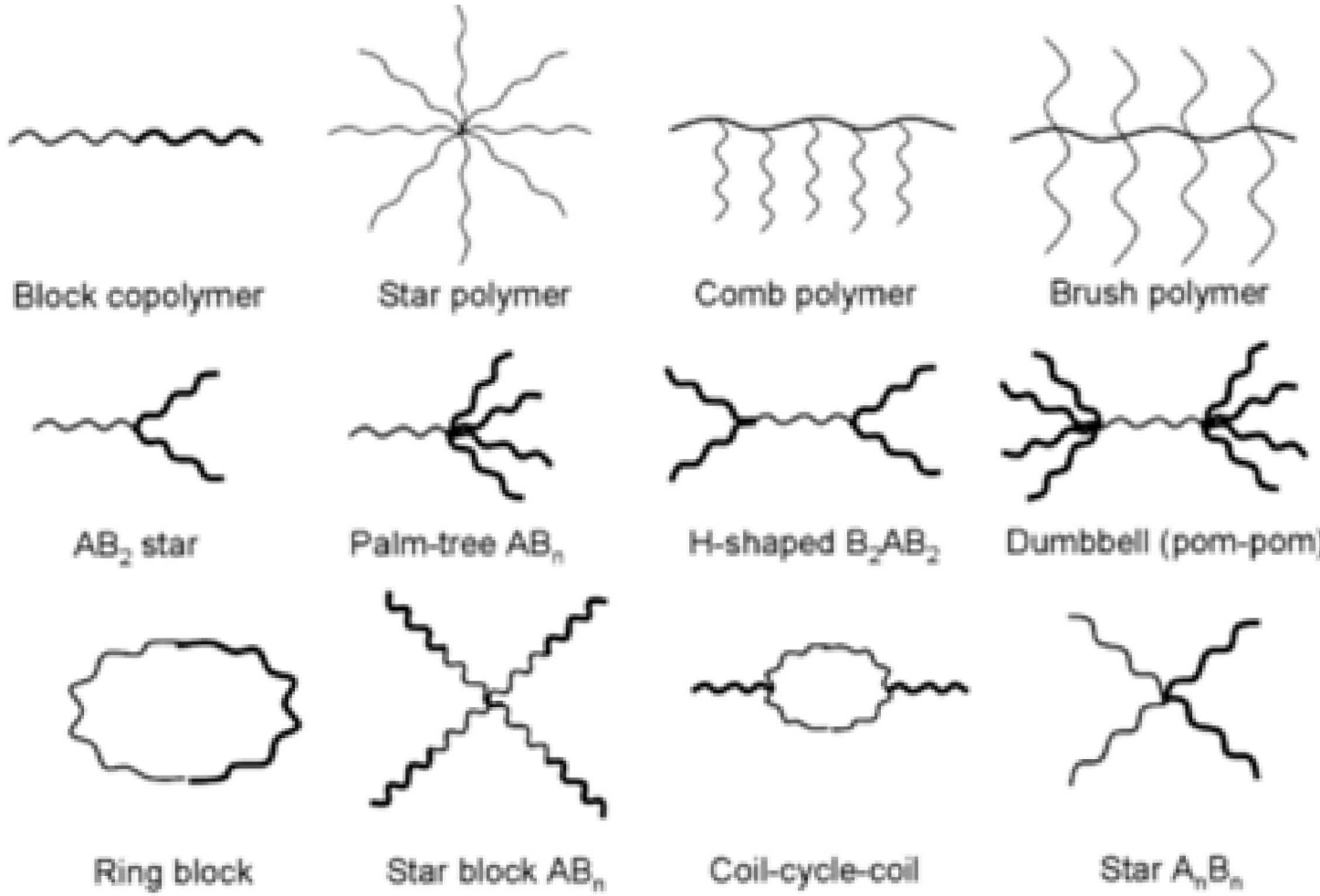


- Linear chains move like a snake

- Rings move by an amoeba-like motion

Polymer Architectures

Polymers not limited to linear chains



Computational Challenges in Polymers

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

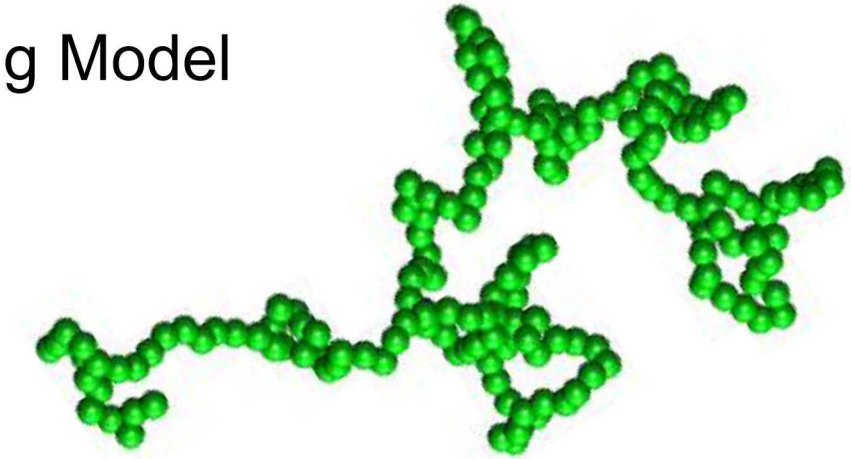
- Chains are Gaussian coils – $R \sim N^{1/2}$
  - Number of chains must increase as $R^3 \sim N^{3/2}$ so polymer chains do not to see themselves through periodic boundary conditions

- 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: ~ 400-1000 particles/processor

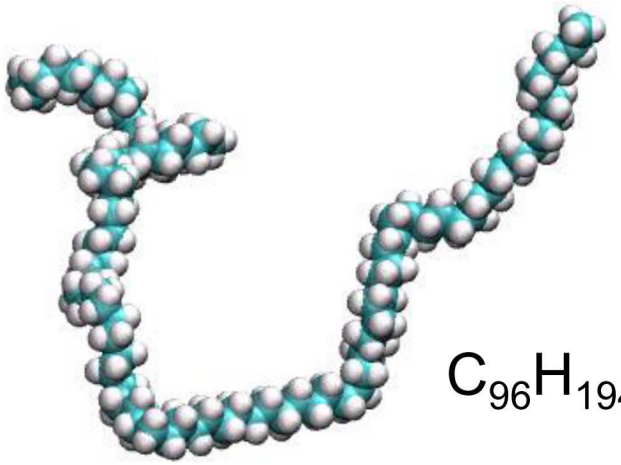
Polymer Simulation Models

- Bead-Spring Model



N=200

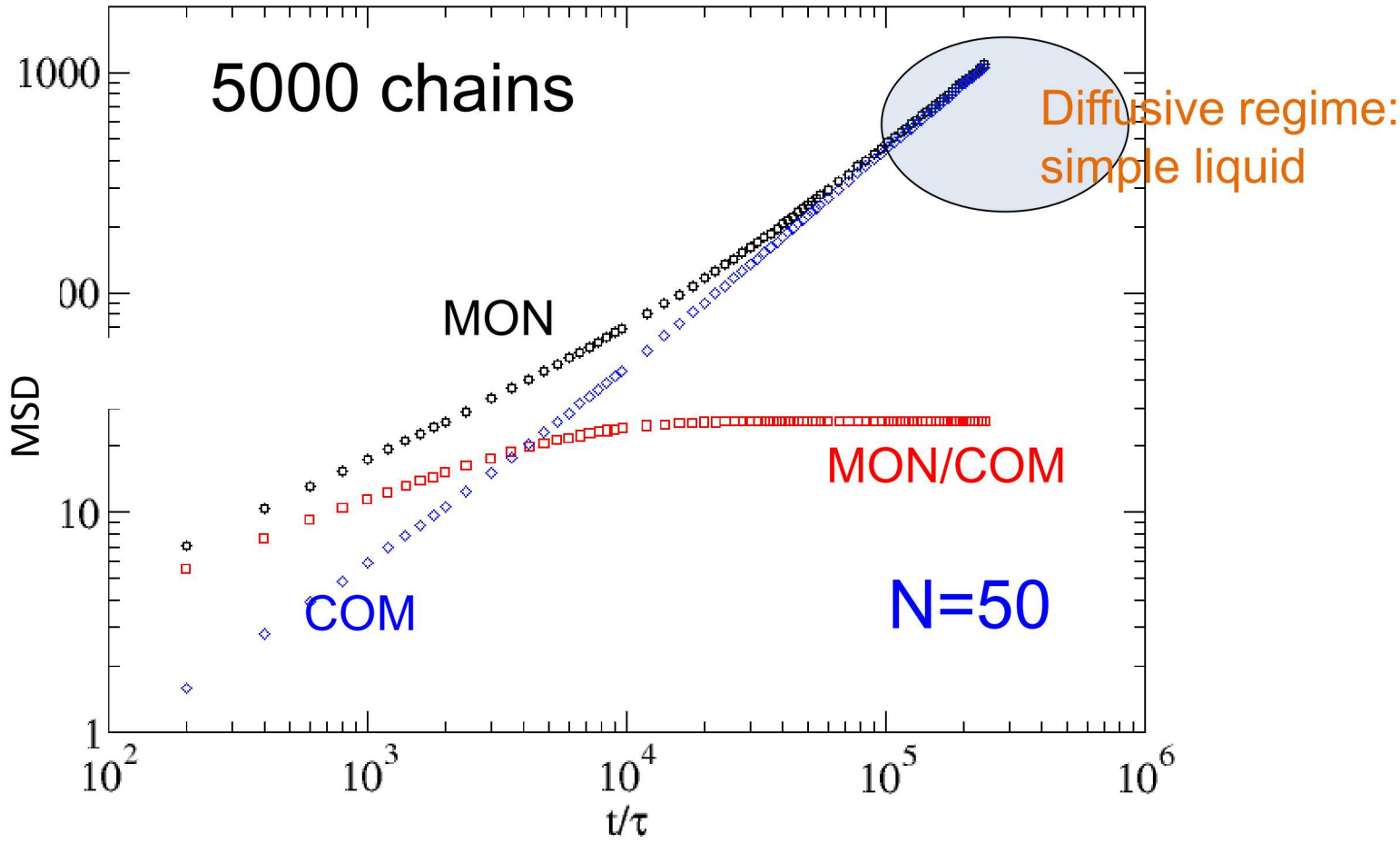
- Atomistic: All Atom



$C_{96}H_{194}$

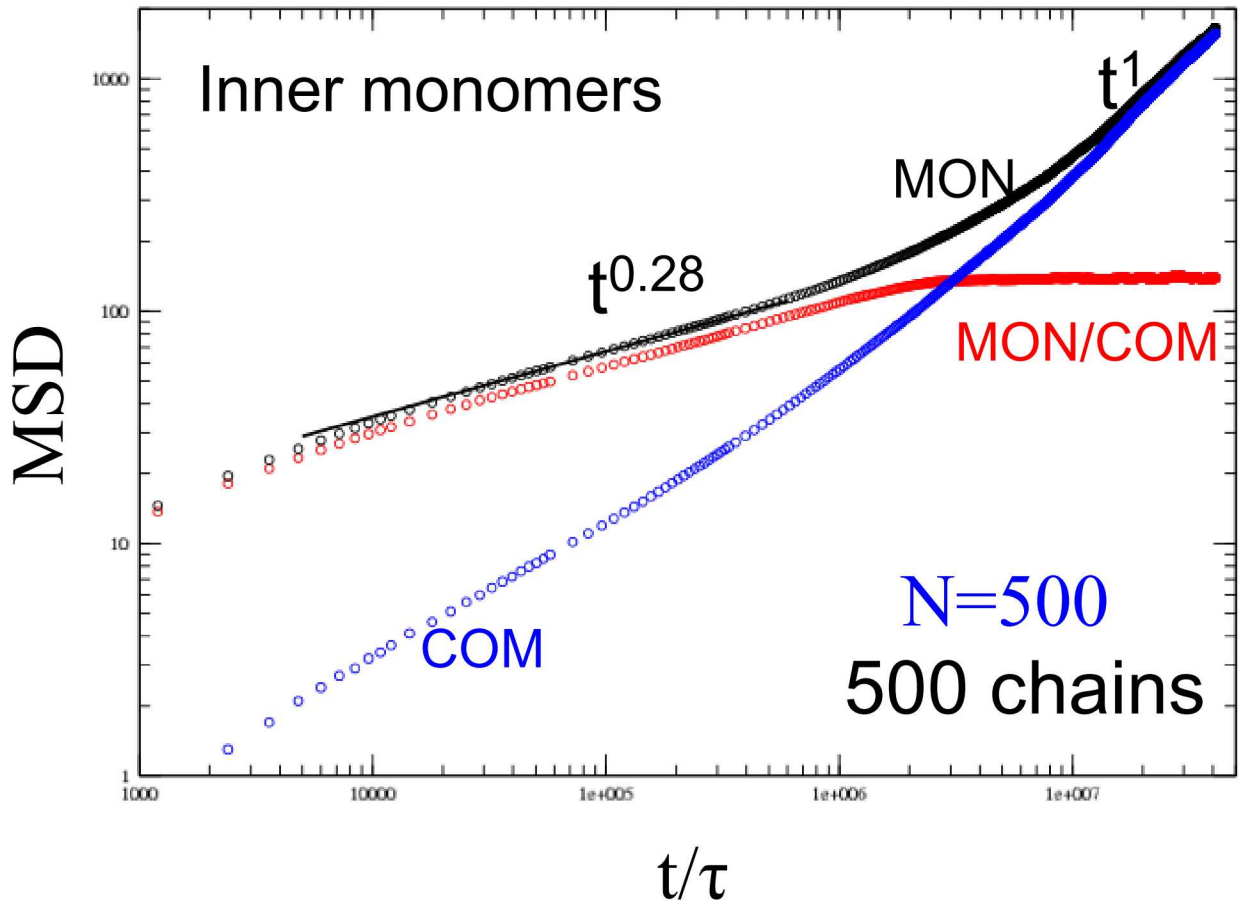
Multiple CH_2 combined into one bead

Motion of Unentangled Polymer



• Once polymer move their own size, unentangled polymers move like simple liquids

State of the Art: Motion of Entangled Polymer



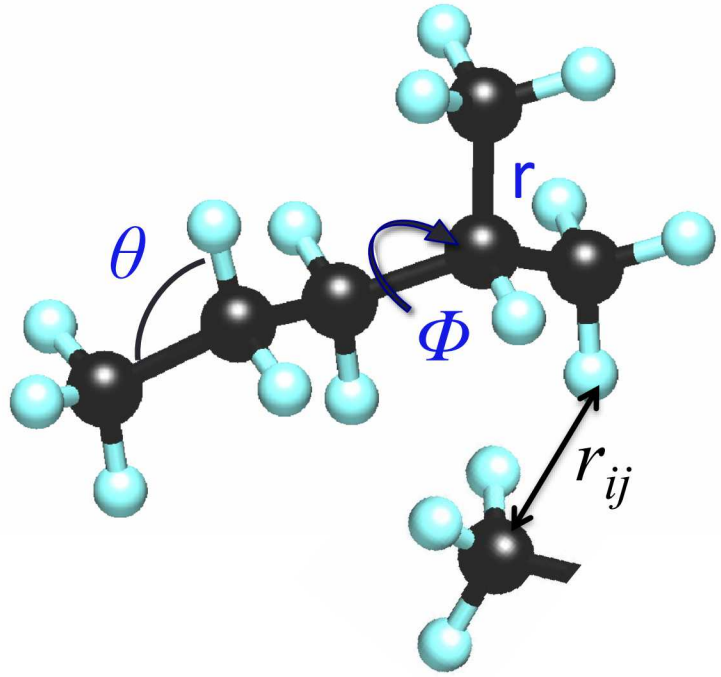
2 million core hours

>10 billion time steps

- $t^{1/4}$ reptation motion is clearly seen at intermediate times
- Second $t^{1/2}$ region still unresolved

Atomistic Simulations

- Bond, Angle, Dihedral
  - quantum chemistry
- Non-bonded van der Waals
  - empirically determined
  - Lennard-Jones 12-6, exp-6
- Coulomb interactions
  - partial/full charge



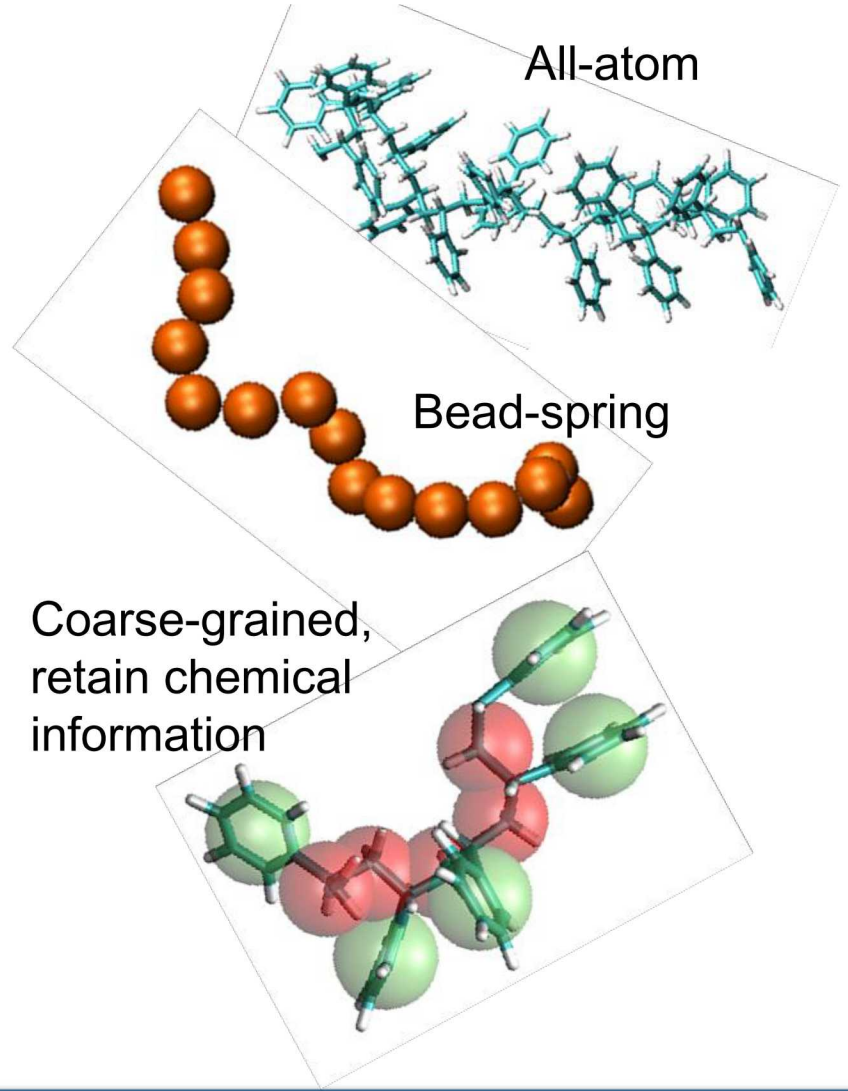
- Time step ~ 1.0-2.0 femtoseconds

  1 ns = 10^6 steps

- Presently limited to 100-1000 ns, 100's thousand – few million atoms

Coarse-Graining of Polymers

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



- Reduced number of degrees of freedom, simpler interaction potentials, reducing the overall computational effort
- Larger time steps (2-20x)
- Reduced effective bead friction due to lower energy barriers and/or a smoother energy landscape
- Back-mapping to fully atomistic model

Degree of Coarse Graining Polyethylene

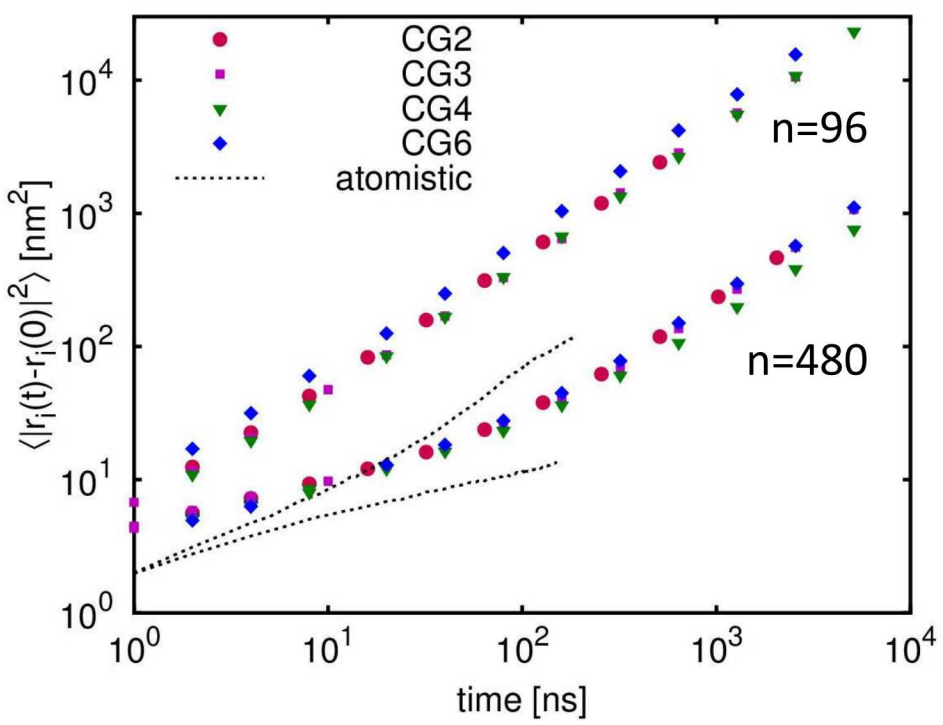
$C_{96}H_{194}$ chain with increasing degree of coarse graining

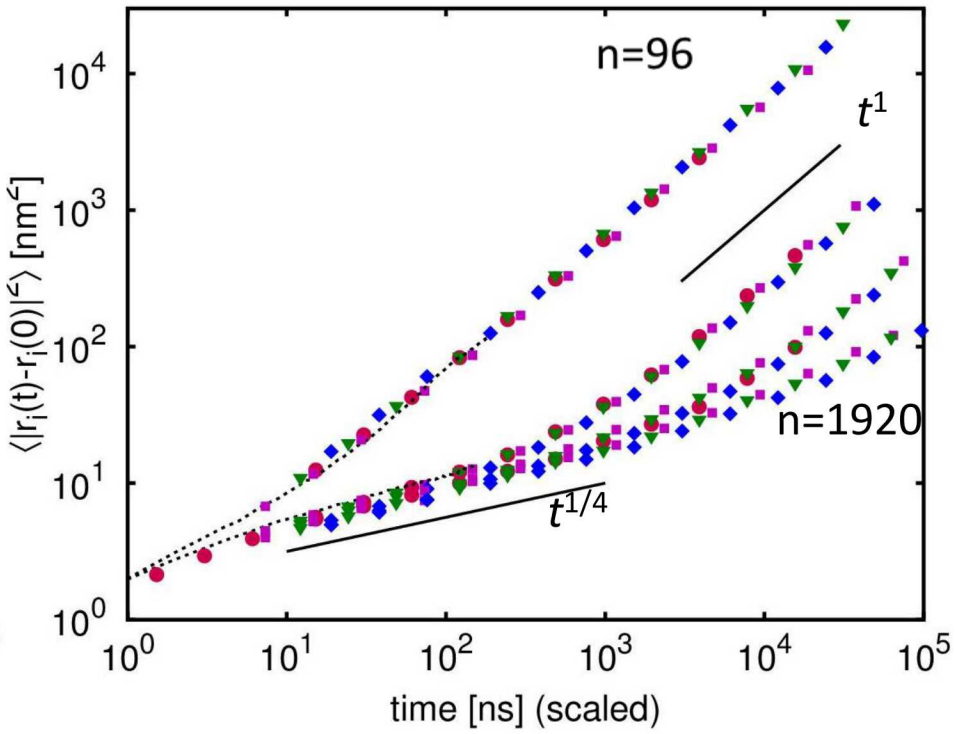
- Largest lengths scales of polymer dynamics are controlled by entanglements
- Shortest time and length scales required to resolve dynamic properties not obvious

- 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);
B. Peters et al, J. Chem Theory Comp 13, 2890 (2017)

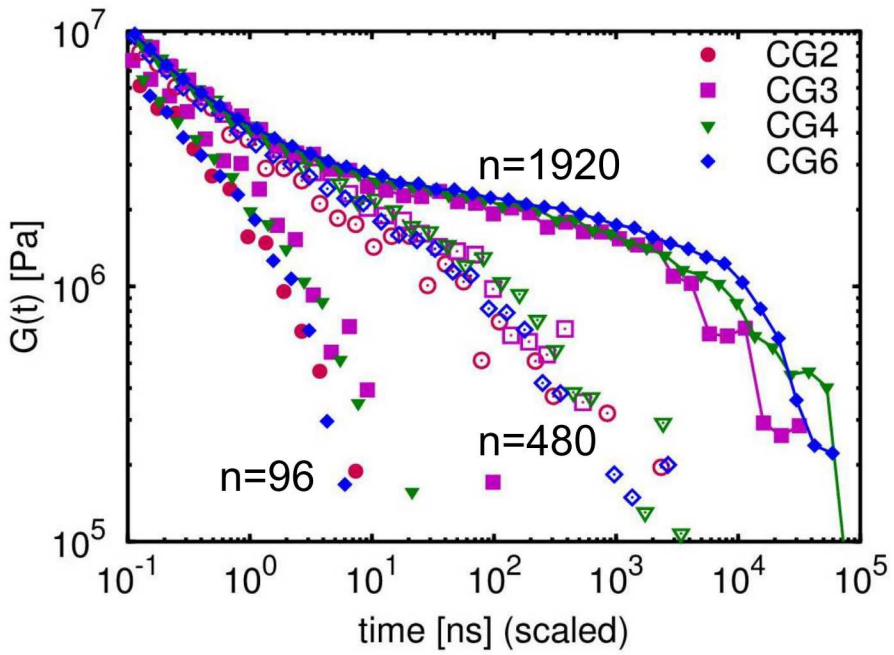
Mapping Dynamics: Coarse Grained to Atomistic

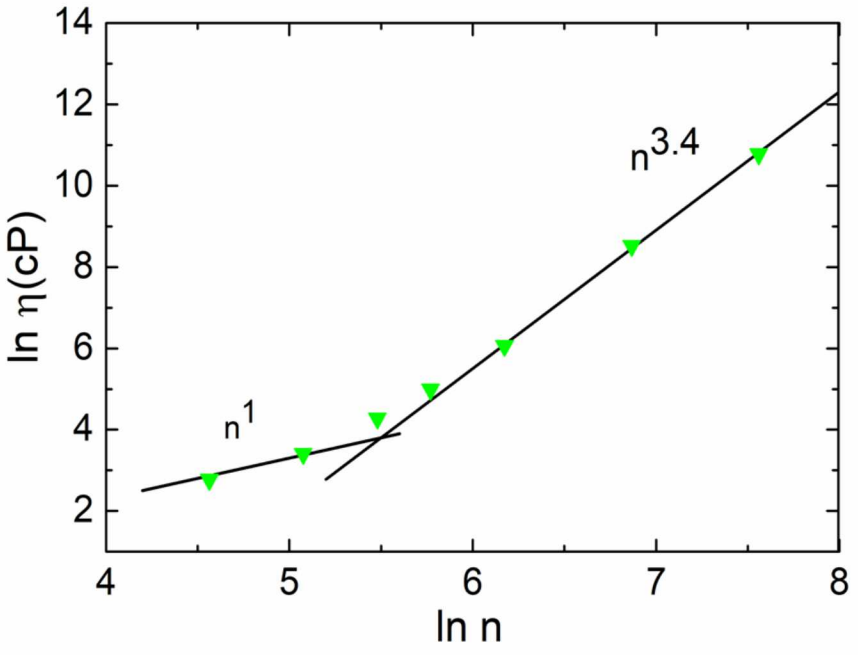




- Coarse graining reduces the number of degrees of freedom in a system, creating a smoother free-energy landscape
- Dynamics of Coarse Grained models 6-12 times faster
- Consistent scaling factor for n = 96 – 1920

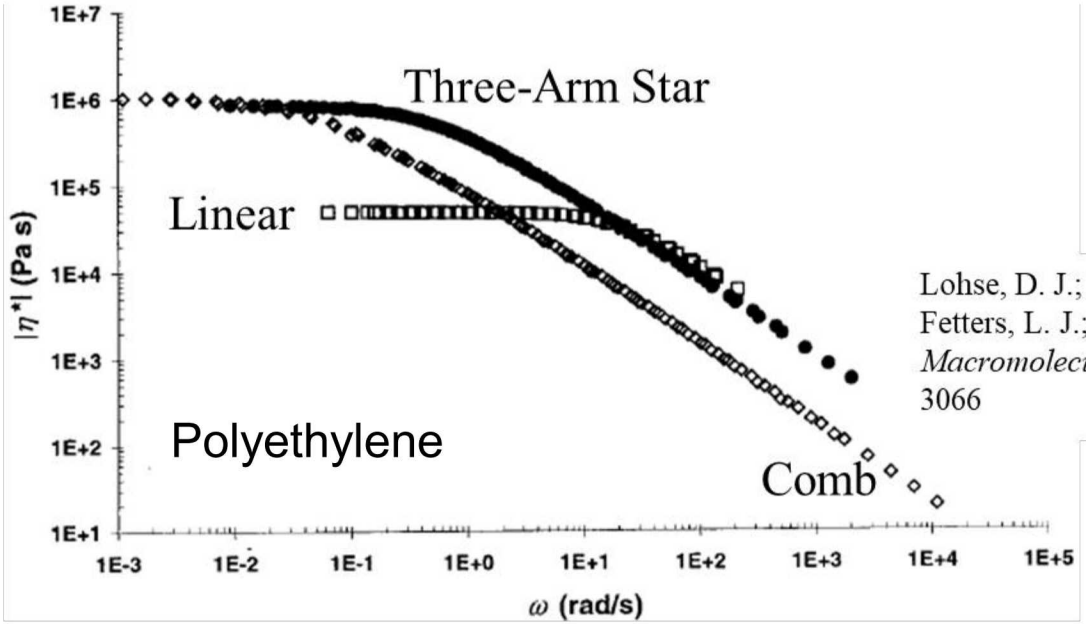
Stress Relaxation and Viscosity





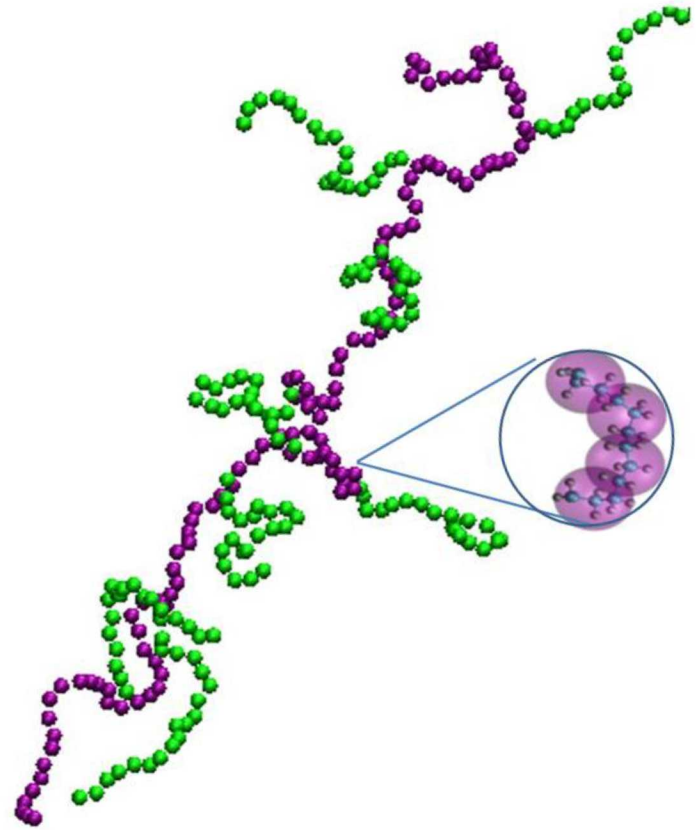
- Longer, more entangled chains form progressively more distinct plateau region
  - Plateau modulus in good agreement with experiment
- Viscosity versus shear rate show shear thinning at high shear rates, crossing over to shear independent regime
- Time and length scales not accessible by atomistic models

Polymer Topology Effects on Rheology



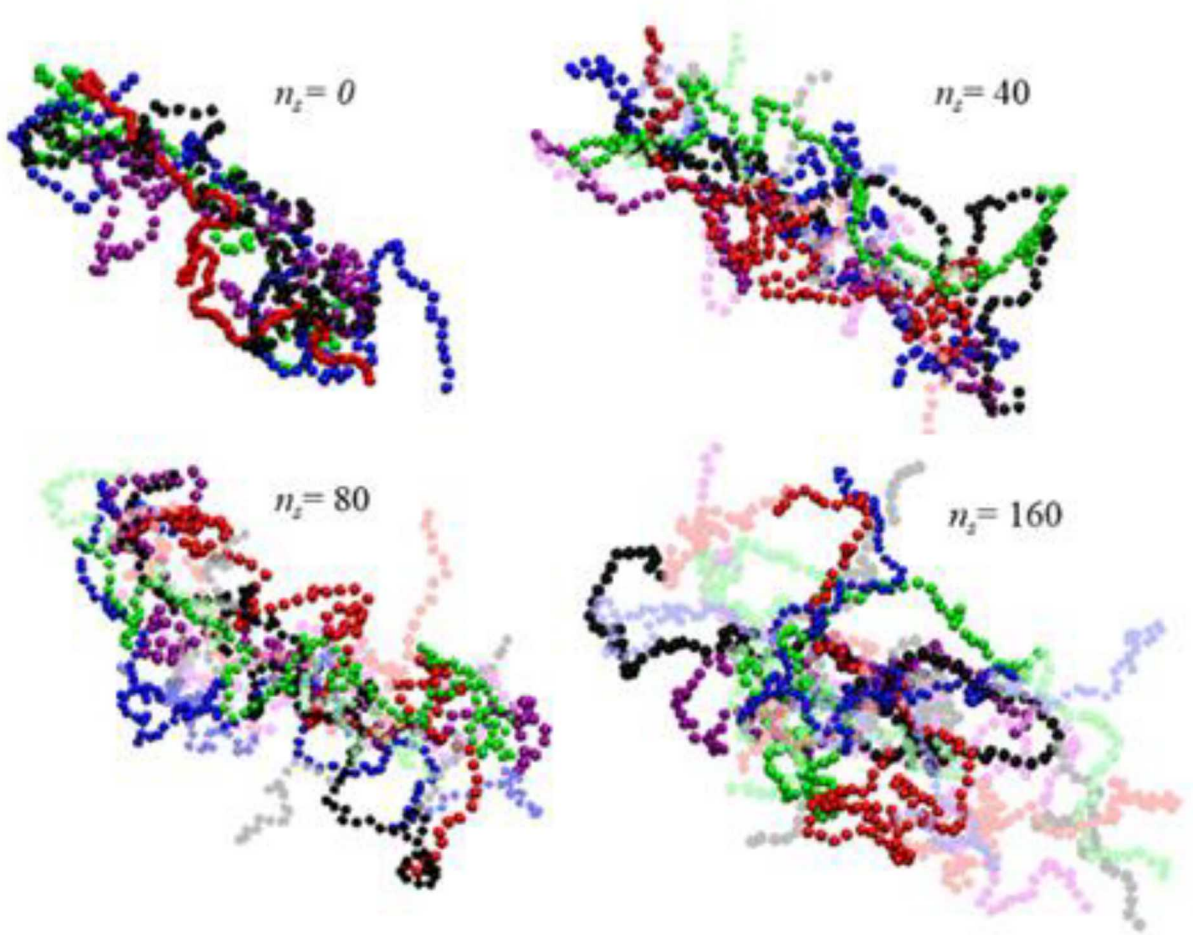
Lohse, D. J.; Milner, S.T.; Fetters, L. J.; Xenidou, M. *Macromolecules.* ***2002****, 35,* 3066

- Branching changes the onset of shear thinning



Coarse grained PE chain with: $\lambda = 4$

Motion of Comb Polymers

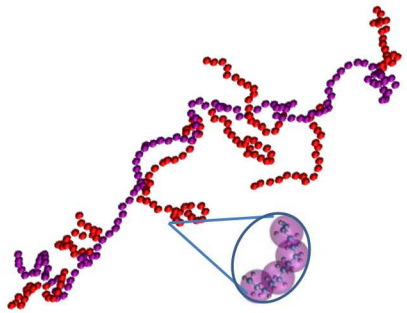


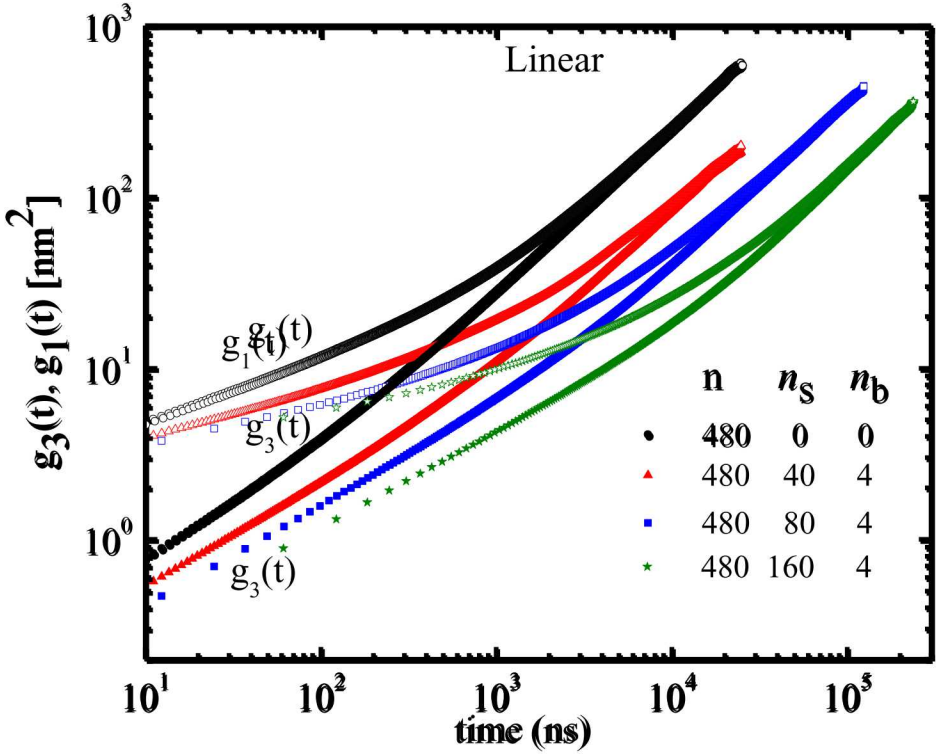
Backbone 120 CG
Beads (480 Carbons)
4 branches

5 Snapshot –
62 ns apart

- Tube diameter Increases with Increasing branch length

Effects of Branch Length on Chain Mobility





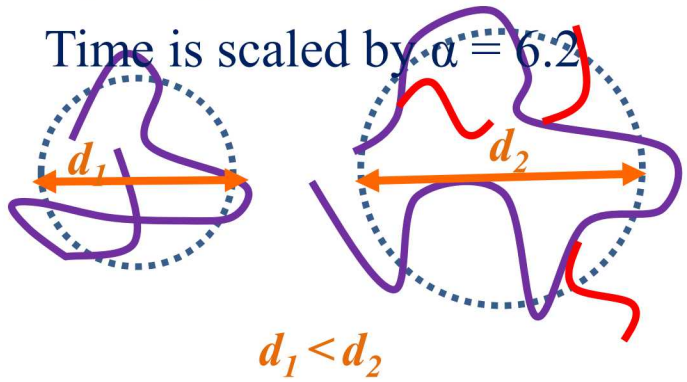
S. Wijesinghe et al., Macromolecules 51, 7621 (2018)

$g_1(t)$ – mean squared displacement (MSD) of the center 4 beads

Constrained polymer chain

$g_3(t)$ – MSD of Center of Mass *reptating in a tube*

Time is scaled by $\alpha = 6.2$

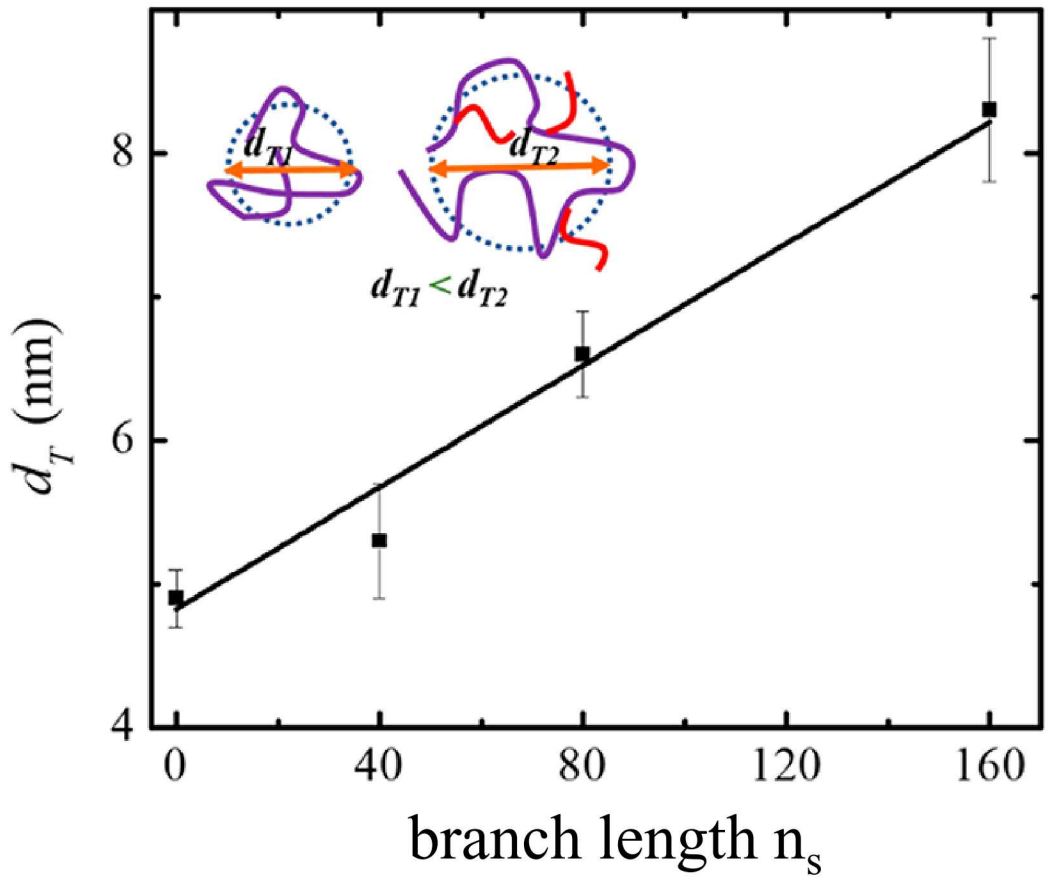


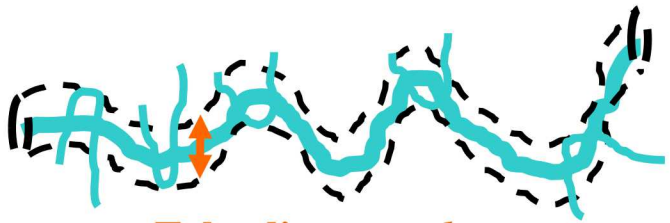
Cross-section of tube for linear and branched polymers

- Increasing branch length results in slower mobility of chains
- Motion of branching points similar to motion of inner monomers

Effects of Branch Length on Tube Diameter

• Extract tube diameter d_T from crossover from early time $t^{1/2}$ Rouse to $t^{1/4}$ reptation regime

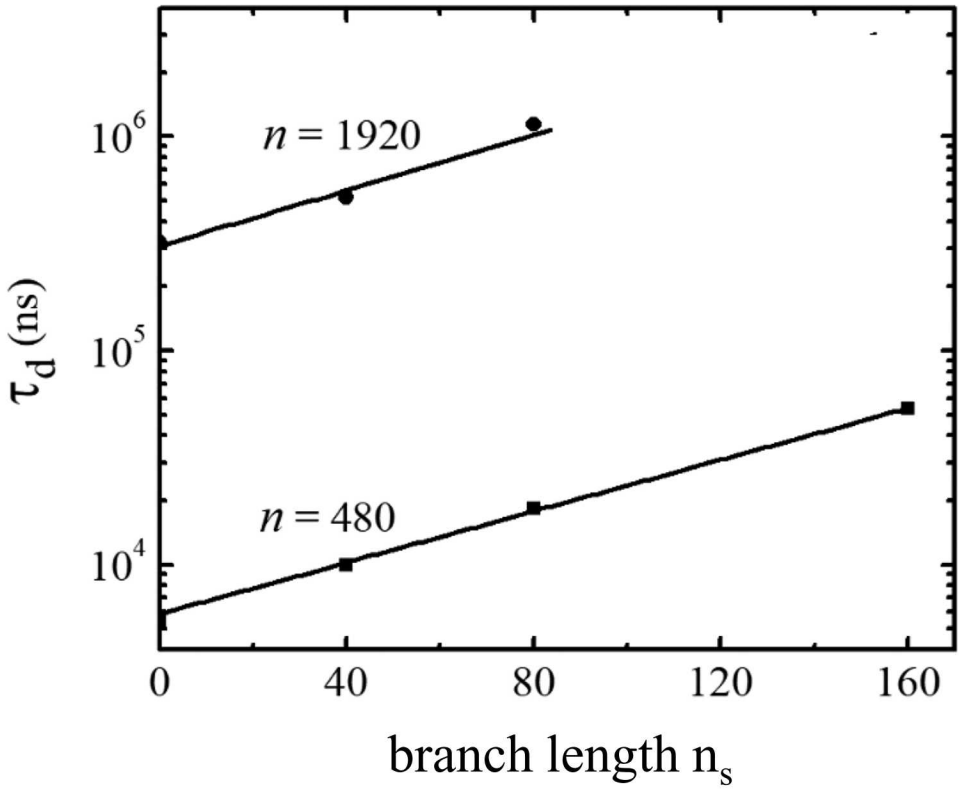


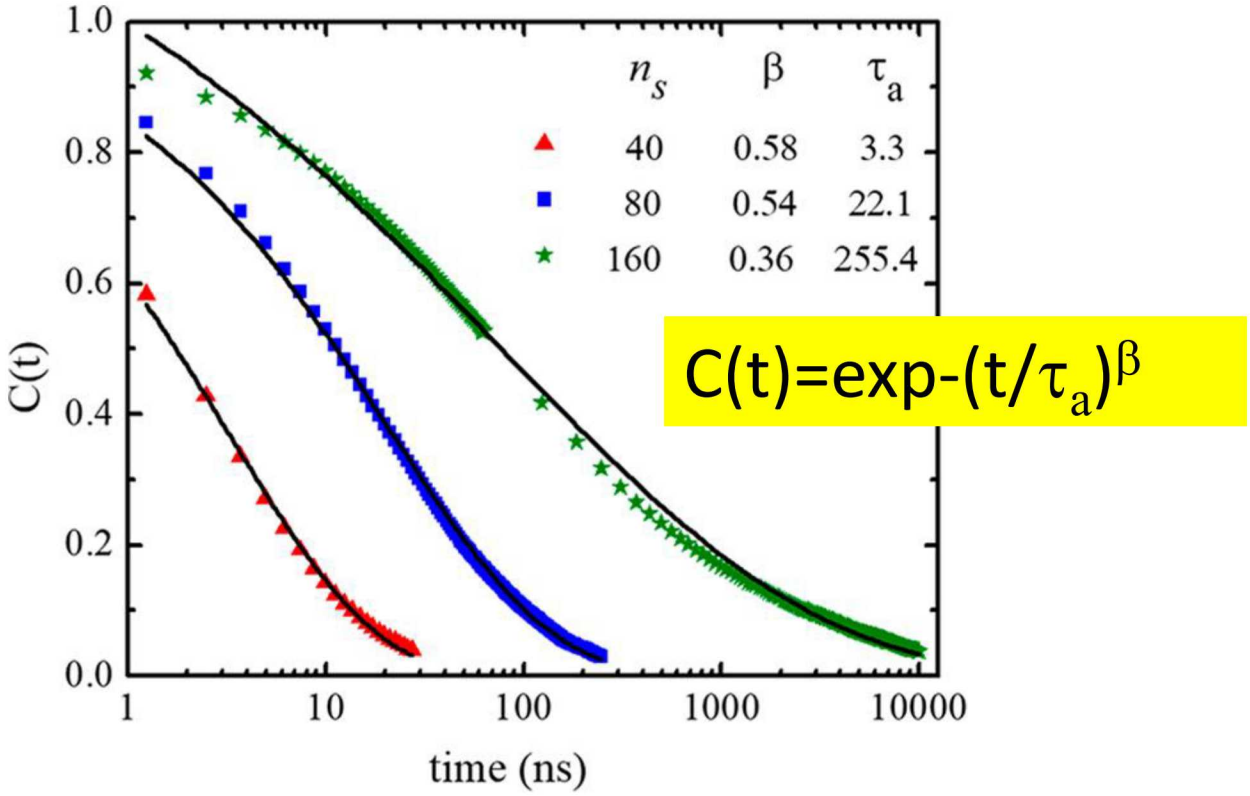


Constrained polymer chain reptating in a tube

Tube diameter increases linearly with branch length n_s

Effects of Branch Length on Chain Relaxation



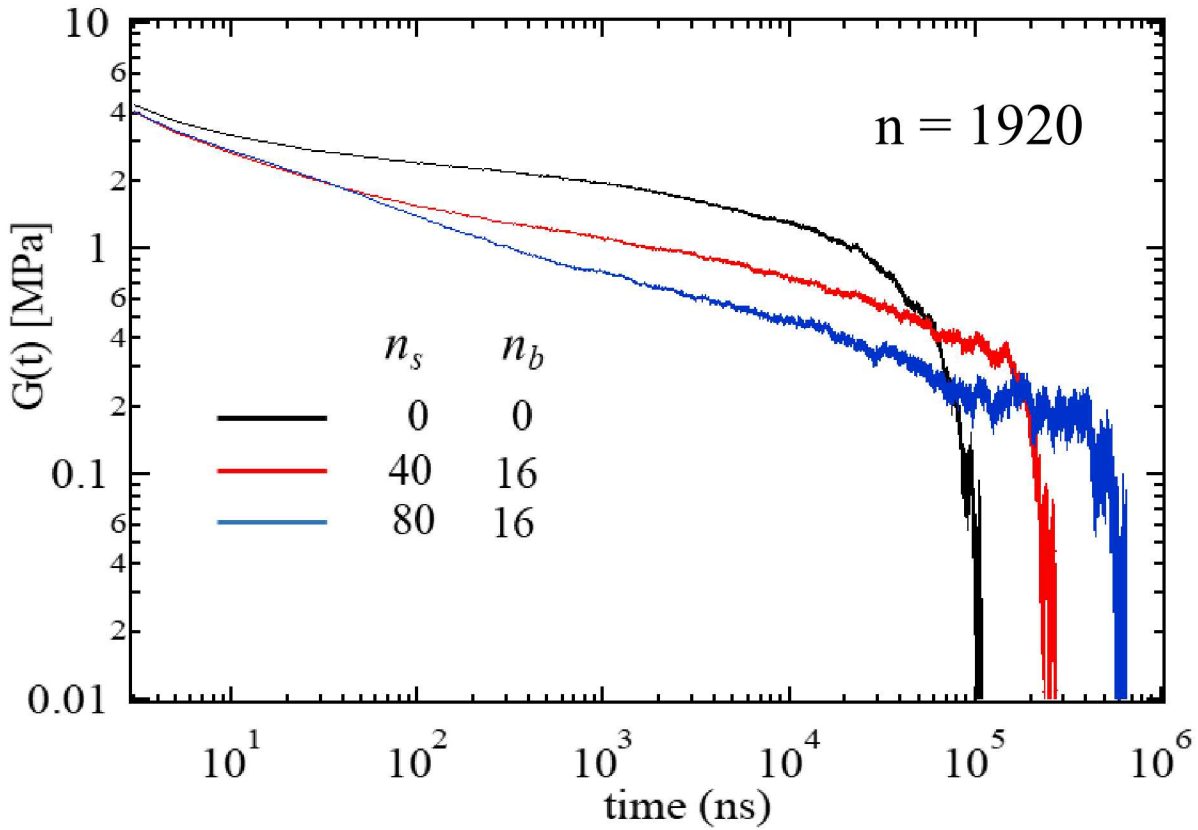


$C(t)=\exp-(t/\tau_a)^{\beta}$

- Diffusive time increases exponentially with branch length

- End-to-end correlation of the branches has wide distribution of relaxation times

Branching Effects on Stress Relaxation



- Stress response function after a small perturbation G(t) can be expressed by the stress autocorrelation function:

$$G(t) = (V/k_BT)\langle\sigma_{\alpha\beta}(t)\sigma_{\alpha\beta}(0)\rangle$$

$\sigma_{\alpha\beta}$ off diagonal element of stress tensor

- Plateau modulus decreases with decreasing branch length n_s consistent with reduction in entanglement length and increase in tube diameter

Summary/Outlook

- Atomistic Simulations ideally suited for phenomena on local scale
  - Present limitations 100-1000's nanoseconds, 10's nanometers
  - Exascale Computing will extend time and length scale significantly

- Simple Coarse-Grained 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

Future Outlook – Exascale and Beyond

- Coarse-Grained Models:
  - Extend beyond focus on chain mobility
  - Stress Relaxation
  - Elongational and Shear Flow
  - Complex Architectures
  - Dispersity
  - Polymer Nanocomposites – Tethered Chains/Shape

- Atomistic Simulations
  - Hundreds ns/day
  - Extend times to 10’s-100’s μs
  - Multi-million atoms simulations

Acknowledgements

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