Dynamics of Entangled Polymers: Using LAMMPS for Large Scale Simulations

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Large Time/Length Scale Simulations

- Many systems one needs large times and length scales
  - Polymers, Membranes, Proteins, Nanoparticles
  - Acceleration algorithms are sometimes useful for structure but rarely for dynamics

- Step 1 Coarse grain – reduces number of atoms by ~ 10 and increase time steps from fs to ps
- Step 2 Build initial state – sometimes easy/sometimes not
- Step 3 Run for a long time on as many processors as possible
  - Number beads > 500/processsor

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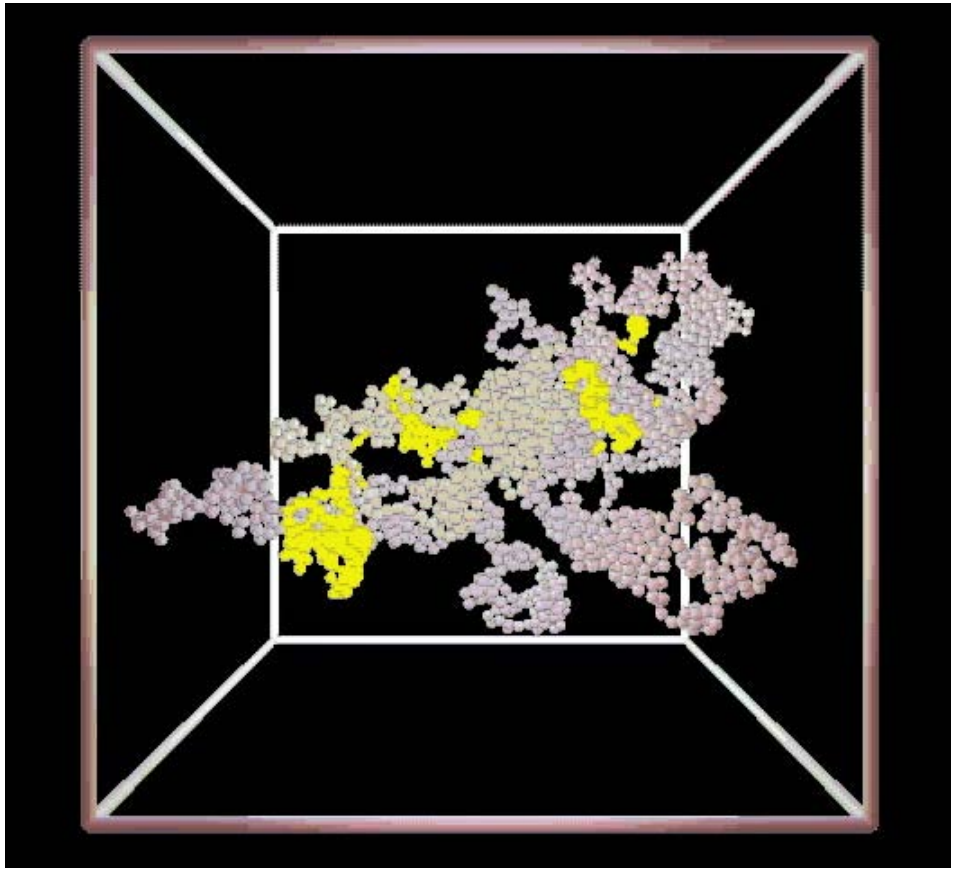
Brute Force – nothing else will do

Why are Polymers Interesting?

- Polymers can simultaneously be hard and soft
  - –Unique Viscoelastic Behavior

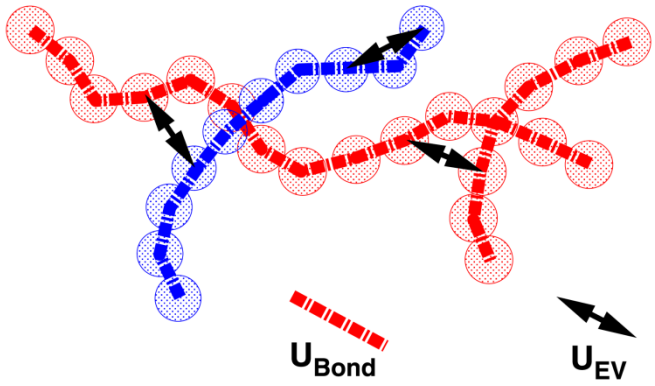


- Motion of a polymer chain is subject to complicated topological constraints

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

$$U_{FENE}(r) = \begin{cases} -0.5kR_0^2 \ln\left(1 - (r/R_0)^2\right) & r \le R_0 \\ \infty & r > R_0 \end{cases}$$

$k=30\varepsilon/\sigma^2$, $R_0=1.5\sigma$

- Energy barrier prohibits chains from cutting through each other – topology conserved
- Chain stiffness can be included by addition of three-body terms
- MD – velocity-Verlet, time step 0.010 - 013τ

Advancement Hardware/Software Past 25 Years

- Modified scalar code (Rahman)
- Vector MD – 4 processor Cray XMP – late 1980's
  - 10^4 monomers – 10 million time steps
- Shared Memory – SGI cluster – 1990's
  - 4-8 processors
- Parallel MD Code – LAMMPS – late-1990's to present
  - 256-2048 processors – Intel and Sun Clusters most recent studies
  - ½ to 1 million monomers – 1-2+ billion time steps
  - 5 million monomers – 300+ million time steps

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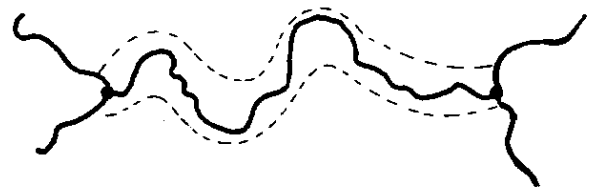
- **WARNING – time_step > 2.14 billion steps bad things happen with LAMMPS**

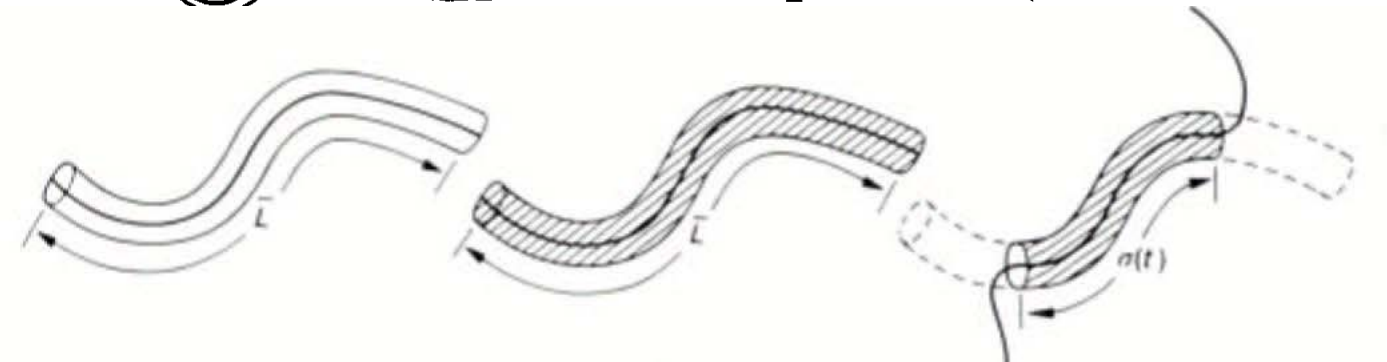
Motion of Polymers

- Statistical Mechanics Approach



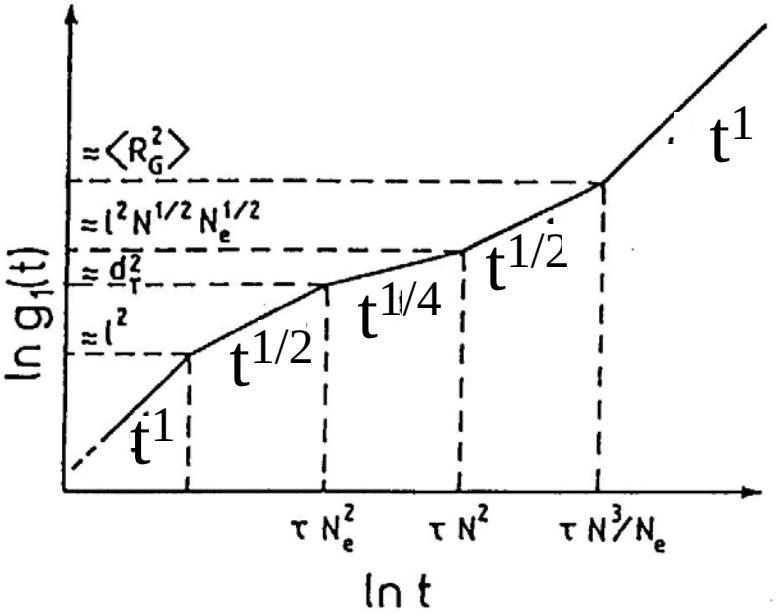
- Tube model (Edwards 1967)

- Reptation (de Gennes, 1971)



Polymer Diffusion

- Simple Liquids
  - $D \sim M^{-1}$, $\eta \sim M$
- Short Polymer Chains ($M < M_e$)
  - Longest relaxation time $\tau_R \sim M^2$
  - Intermediate $t^{1/2}$ time regime in mean square displacement
  - $D \sim M^{-1}$, $\eta \sim M$
- Long Polymer Chains ($M > M_e$) - Reptation



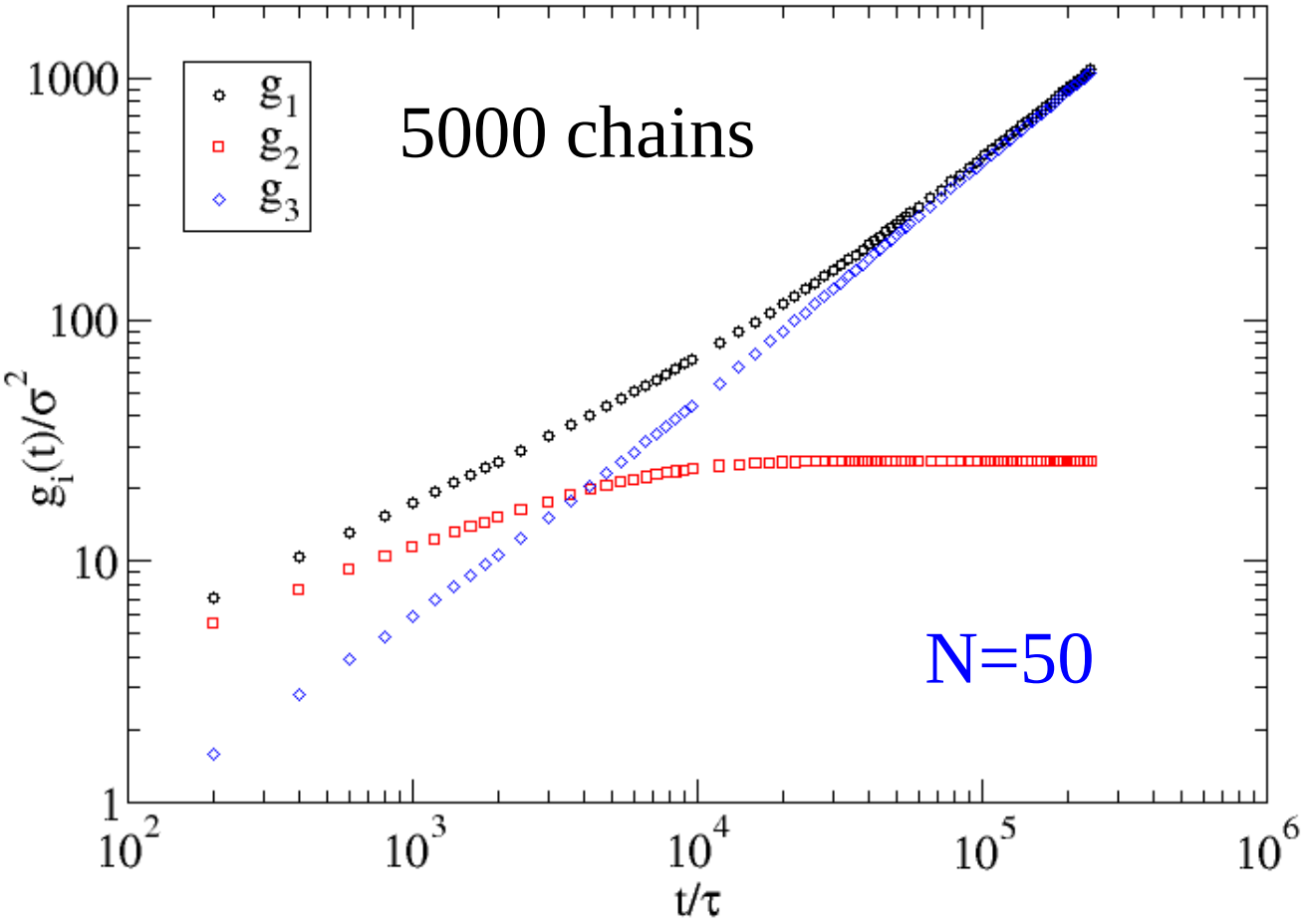
$D \sim M^{-2}$

$\eta \sim M^3$

$\tau_d \sim M^3$

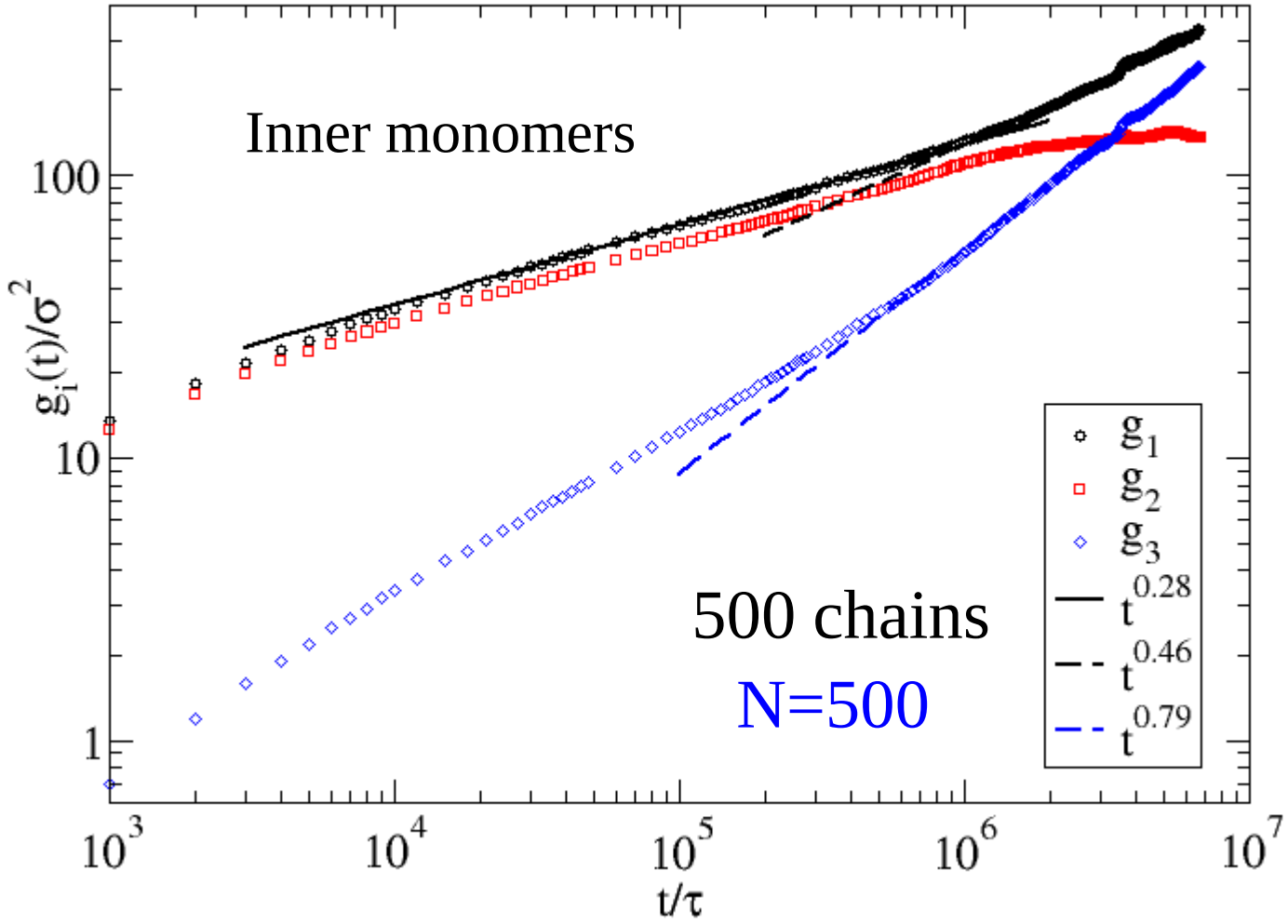
Characteristic signature – intermediate $t^{1/4}$ regime

Displacement of Unentangled Polymer



• Intermediate $t^{1/4}$ regime of mass uptake corresponds to Rouse regime of mean squared displacement

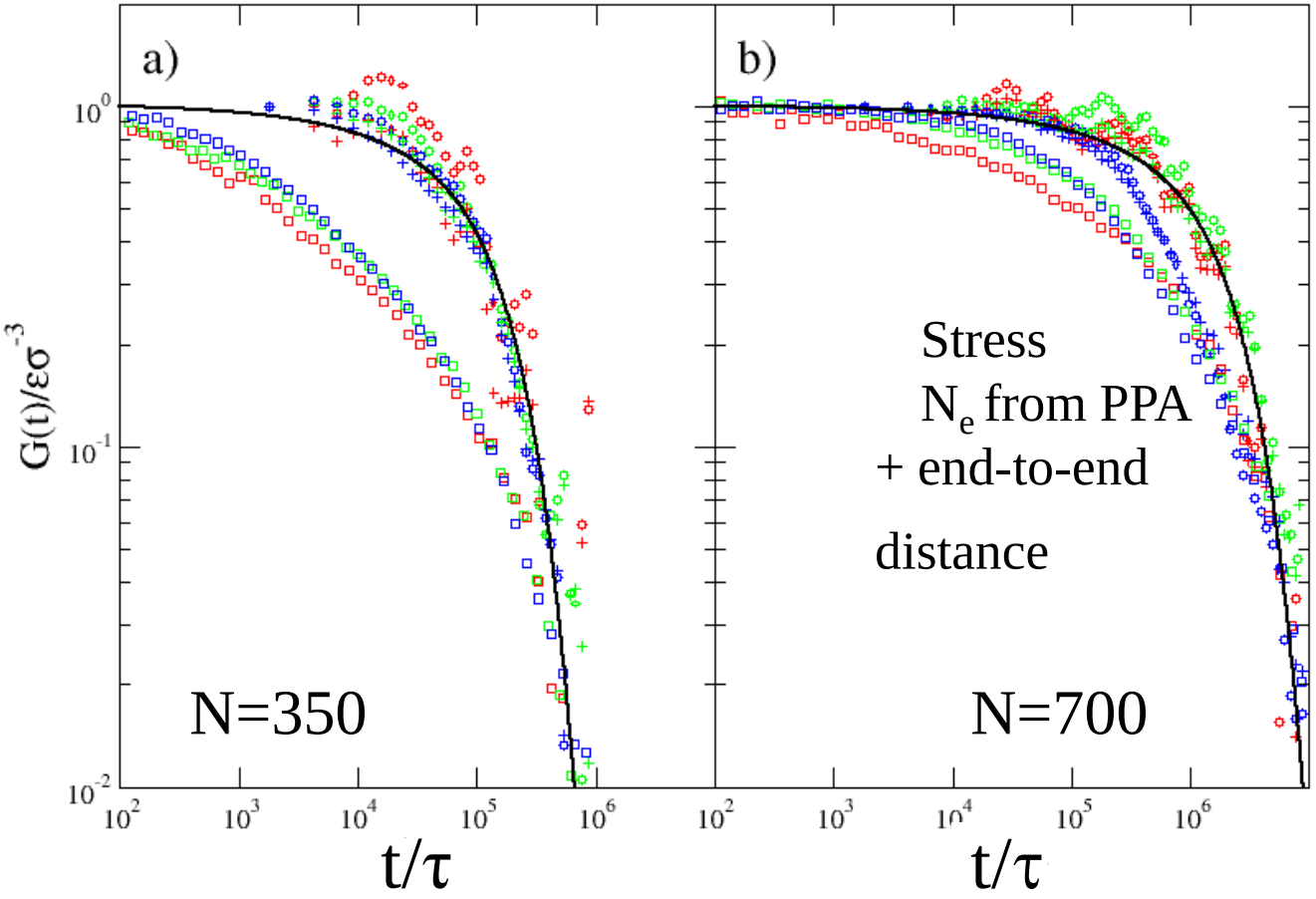
Displacement of Entangled Polymer



- 100, 000 processor hours

Stress Relaxation - Melt

- Relaxation after elongation – λ= 2, 3, 4 (red, green, blue)



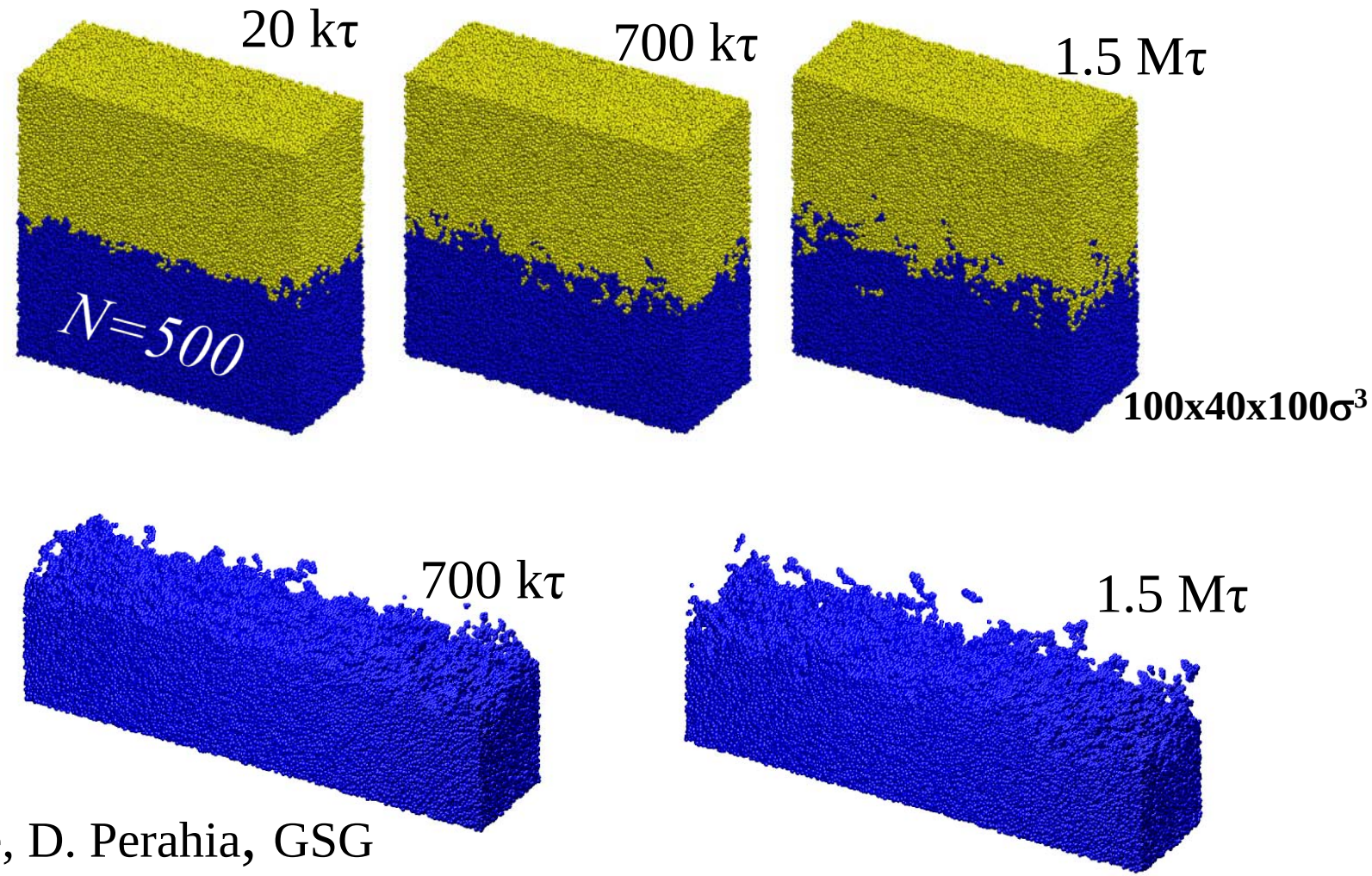
- N=1000
  – similar results
- N=3500
  – reach plateau

C. Svaneborg *et al.*, PRL (submitted)

- Relaxation time independent of λ. same terminal relaxation time for all 3 quantities
- Experimental Strains – λ=1.01 to 1.05

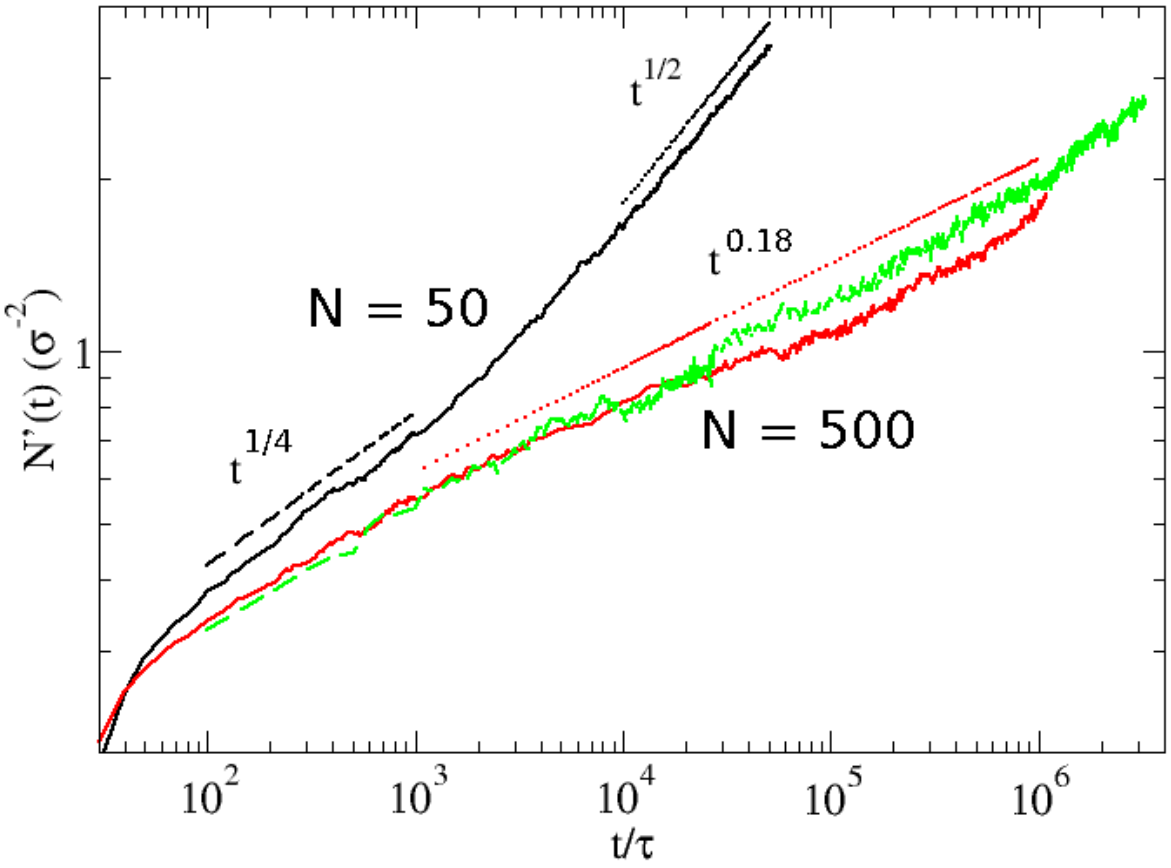
Self-Healing of Polymer Films

- Development of Entanglements Across an Interface



F. Pierce, D. Perahia, GSG

How Fast Does a Crack Heal?



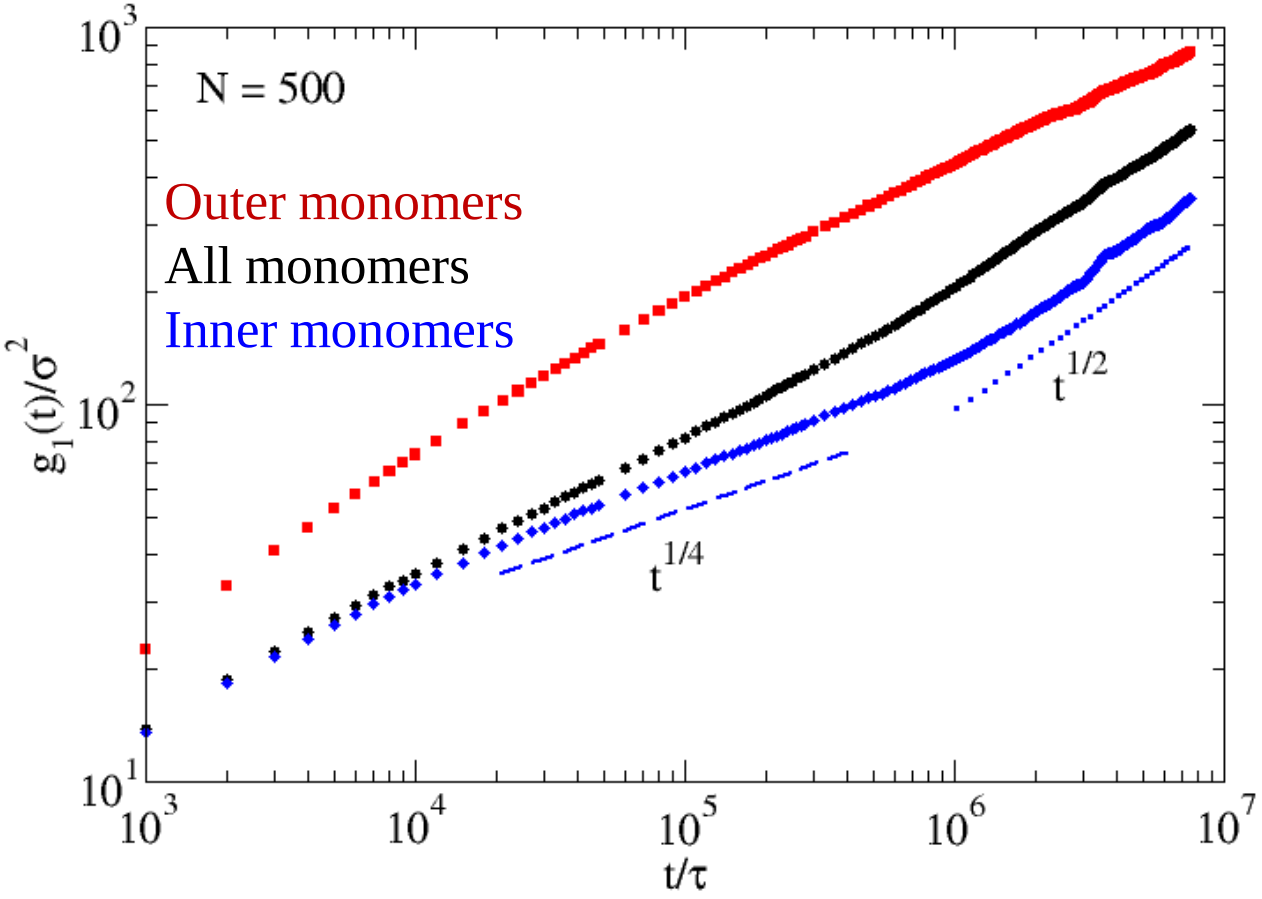
4.8 million monomers

3.5 million steps/day 1024 cores

Longest run – 2.5 million node hours

Mass Uptake, Penetration Depth $z \sim \langle r(t)^2 \rangle^{1/2}$

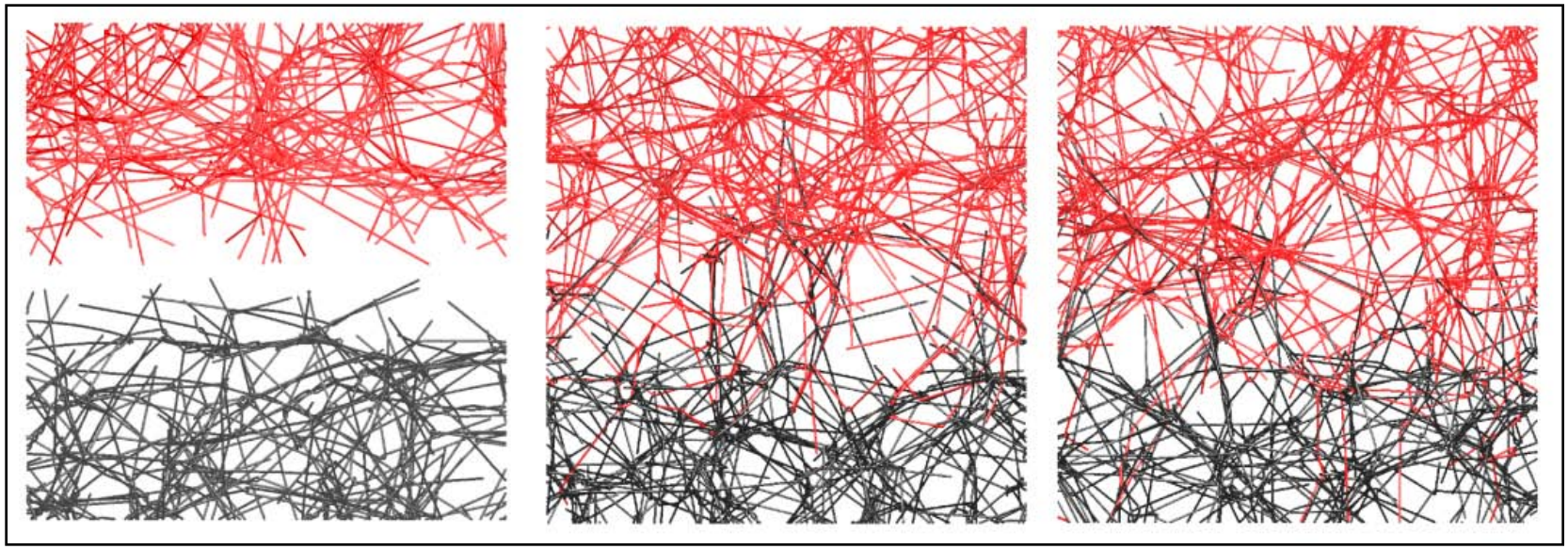
Healing Depends on Motion of Chain Ends



- Chain ends move much faster, resulting in much faster self-healing then predicted by theory

Entanglements at Interface

- Primitive Path Analysis
  - Contact all chains simultaneously with ends fixed
  - (n_{dec} – 1) new beads are placed between adjacent beads on the original chains and process repeated - n_{dec}=4



R. Everaers *et al.*, Science **303**, 823 (2004); R. Hoy and G. S. Grest, Macromolecules **40**, 8389 (2007).

Future Directions

- Outlook for computer modeling is exciting
  - Faster, cheaper computers
  - Efficient parallel MD codes
- Larger Systems, Longer Chains, Longer Times
- Smaller strain, shear rates
  - Viscosity
  - Relaxation after shear
- Constraint Release - Polydispersity
- Semidilute polymers – explicit solvent
- Primitive Path Dynamics – Melts/Networks
- Branched Polymers, Stars, ….

Acknowledgement

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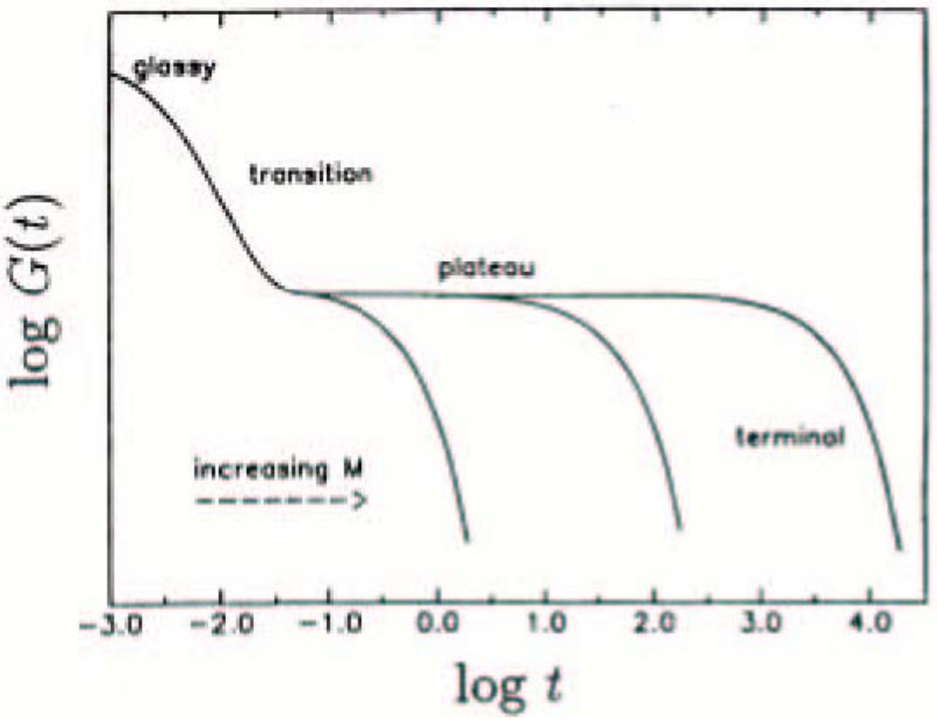
- Center for Integrated Nano Technologies – Sandia
- New Mexico Computer Applications Center

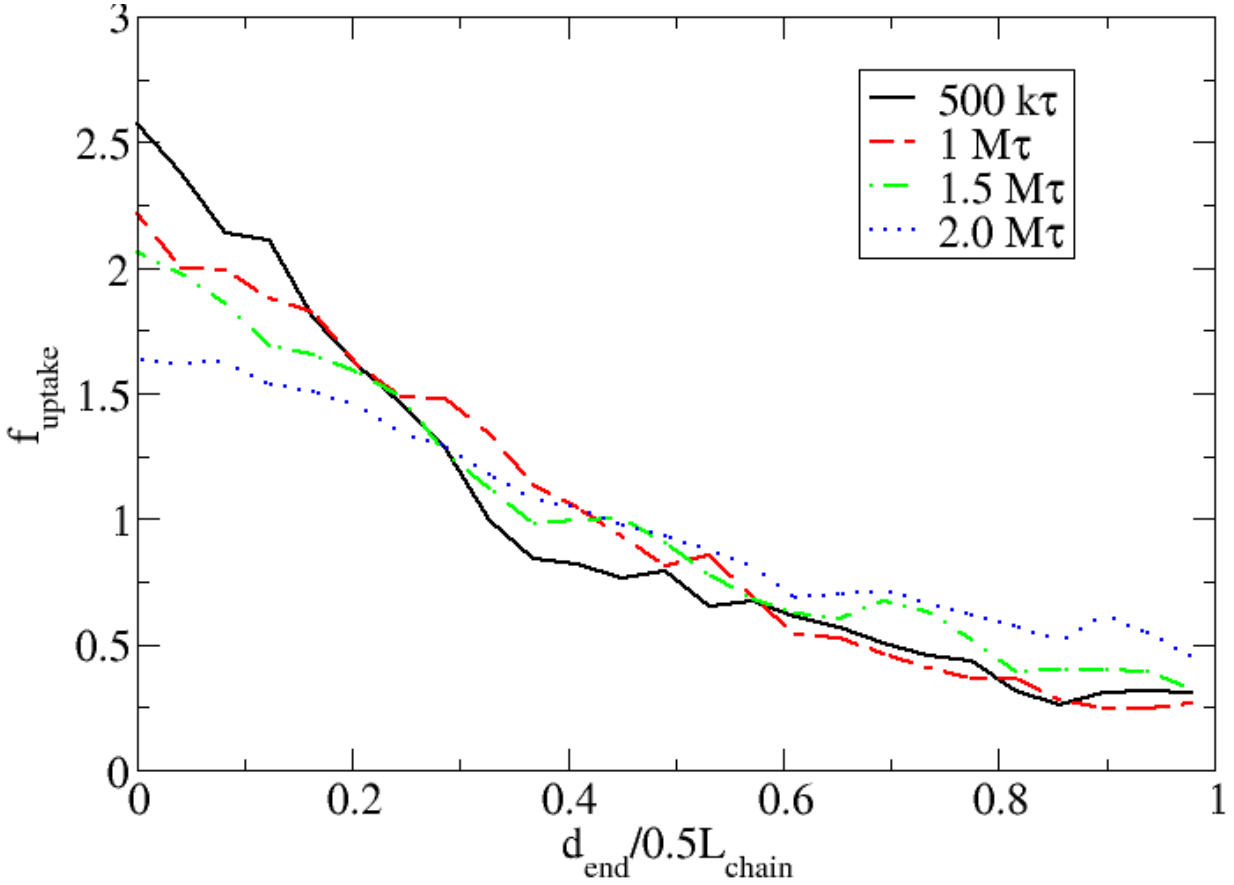
Viscoelasticity of Entangled Polymer Melt



Stress Relaxation *G(t)* after strain

- Macroscopic
  - – Intermediate frequency, time polymer melt acts as a solid
  - – Long time, low frequency polymer acts as a liquid
- Microscopic
  - – Gaussian coils, $R \sim N^{1/2}$
  - – Stress is due to entropy loss of stretched chains
  - – Polymers as "entropic springs"
  - – Stress relaxation due to Brownian motion of topologically constraint chains

What contributes to interdiffusion?



- Chain ends dominate early time interdiffusion
- Rouse motion of chain ends leads to faster mass uptake