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Nanoparticle Diffusion in a Polymer Matrix

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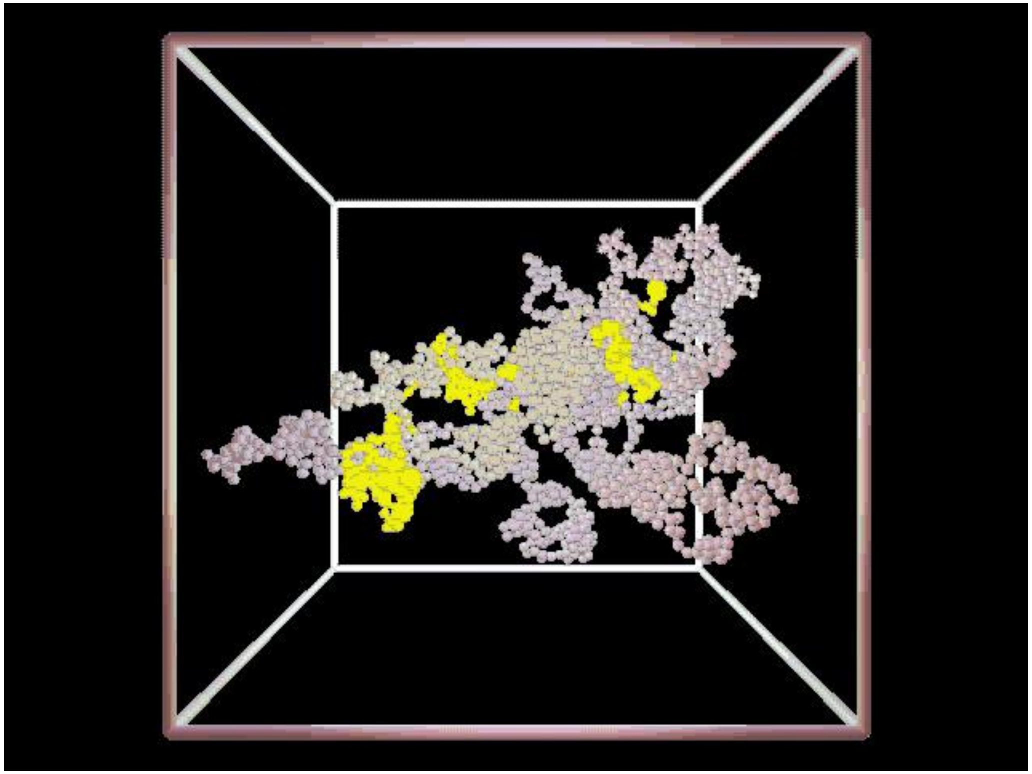
Outline

- Unique Properties of Entangled Polymers
- Computational Challenges
- Dynamics of Linear Polymers
- Dynamics of Ring Polymers
- Polymer Nanocomposites
- Future Directions

Why are Polymers Interesting?

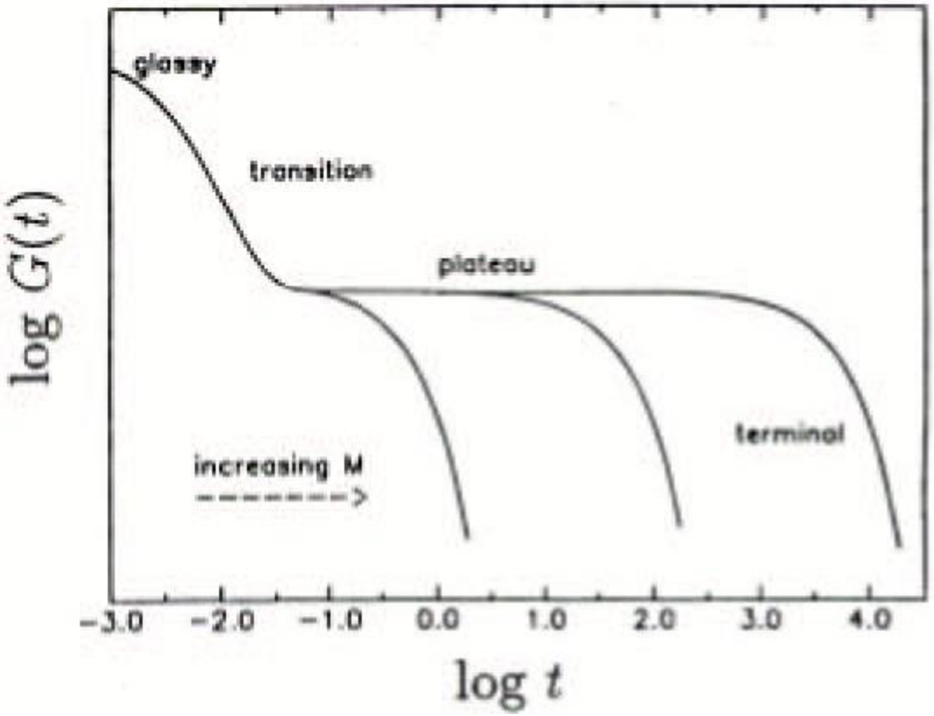
- Polymers can simultaneously be hard and soft
    - –Unique Viscoelastic Behavior



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

Entangled Polymer Liquids

Viscoelastic Response



Stress Relaxation 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 ~ $N^{1/2}$
- Stress is due to entropy loss of stretched chains
- Polymers as "entropic springs"
- Stress relaxation due to Brownian motion of topologically constrainted chains

Computational Challenges

- 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

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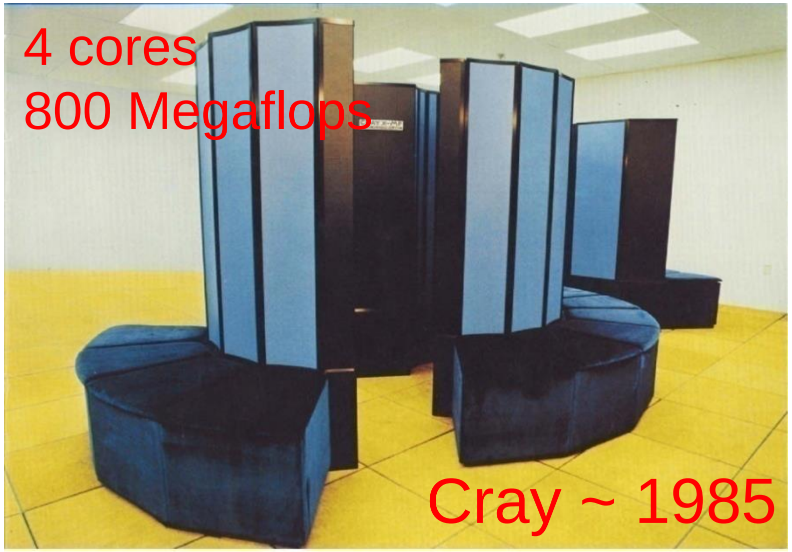
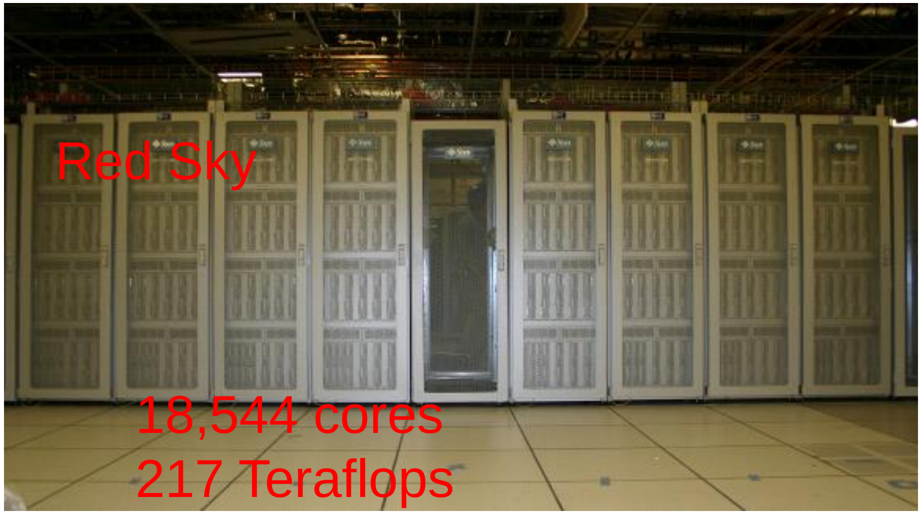
- Number of processors limited: ~1000 particles/processor

- Software/hardware advances have been significant

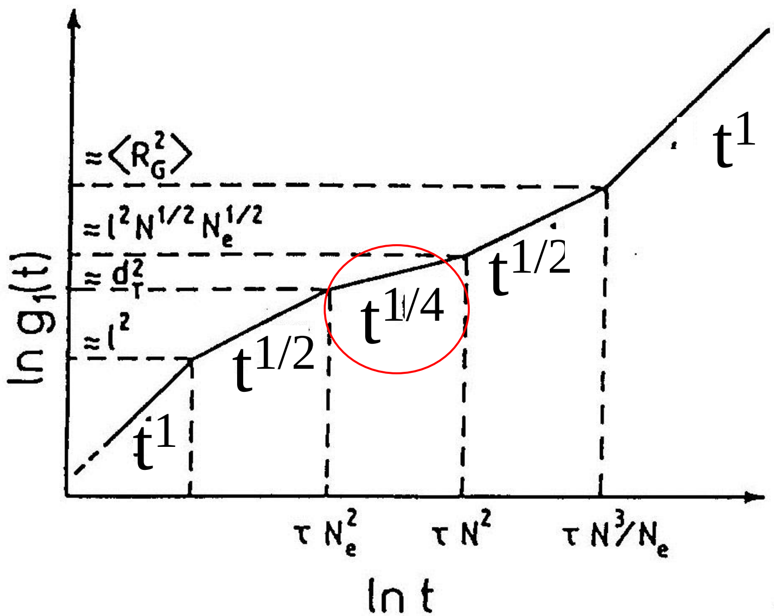
Toys for the Simulator





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



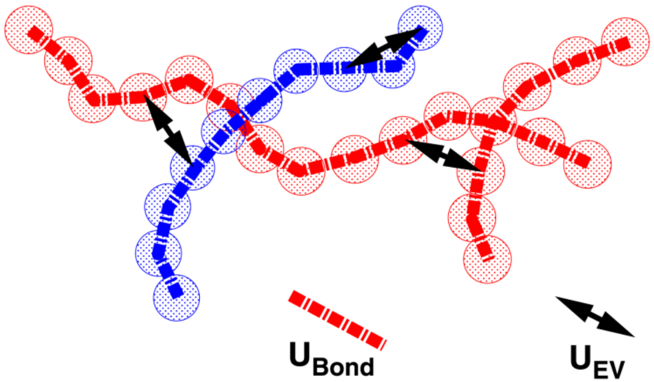
$D \sim M^{-2}$

$\eta \sim M^3$

$\tau_d \sim M^3$

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

Bead-Spring Model



- Short range - excluded volume interaction

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

- Bonded interaction - FENE spring

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

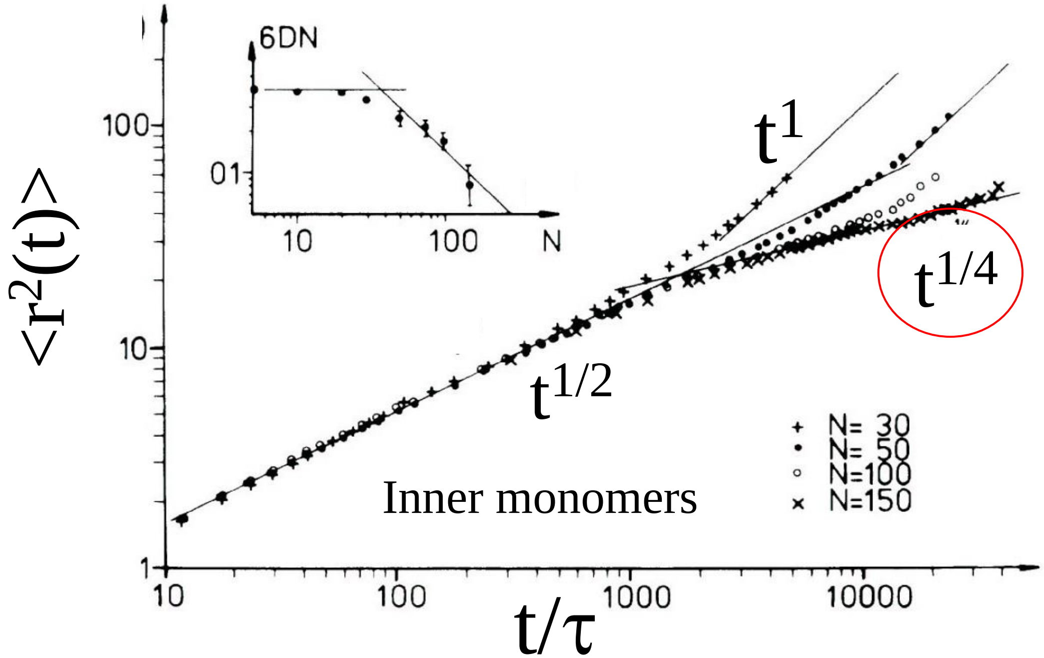
$k=30\varepsilon/\sigma^2$, $R_o=1.5\sigma$

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

Polymers do Reptate!

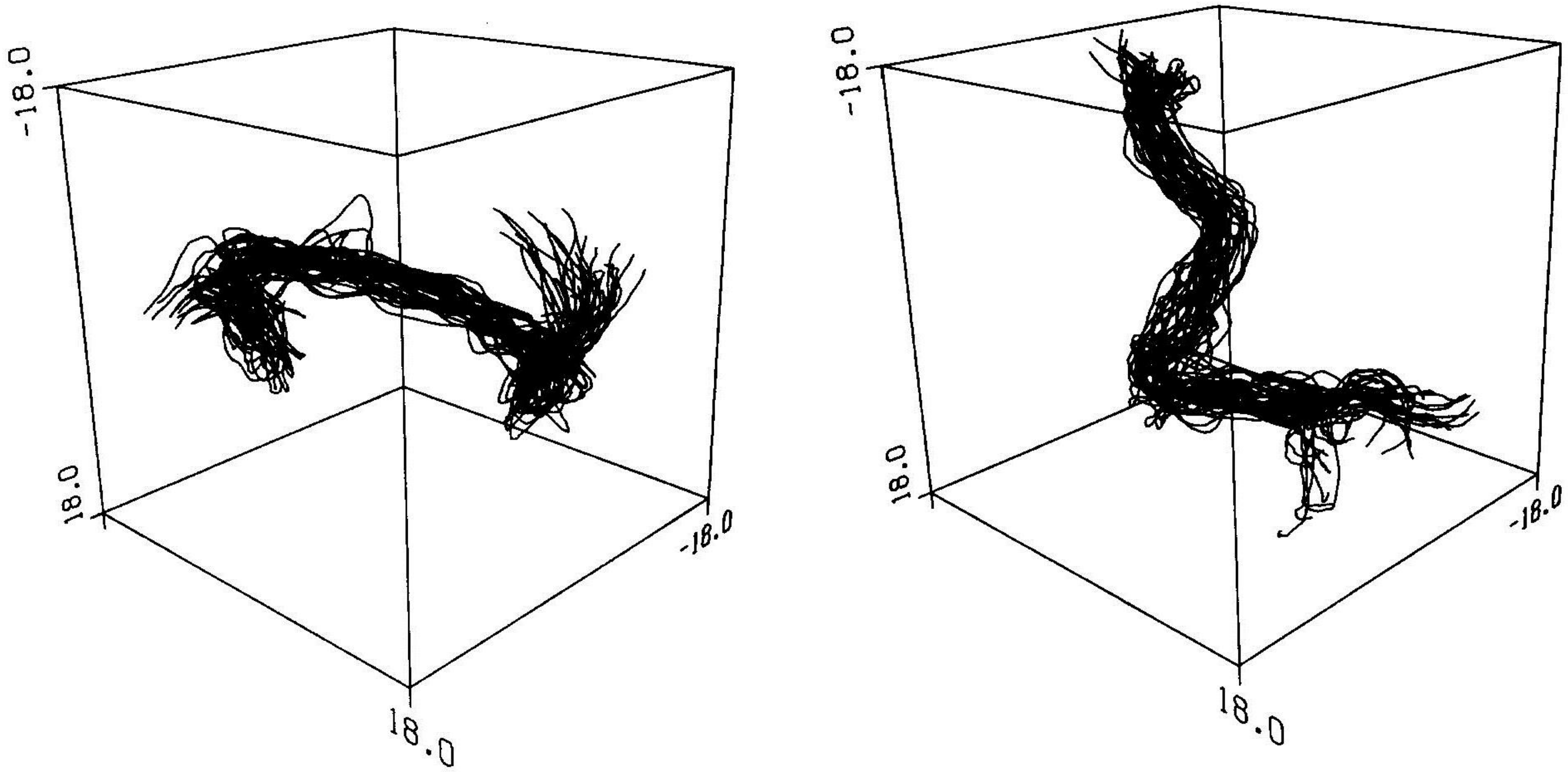


- $t^{1/4}$ reptation regime for N > 100
- First direct evidence from simulation or experiment

Kremer *et al.*, PRL 61, 566 (1988); Kremer and Grest, JCP 92, 5088 (1990)

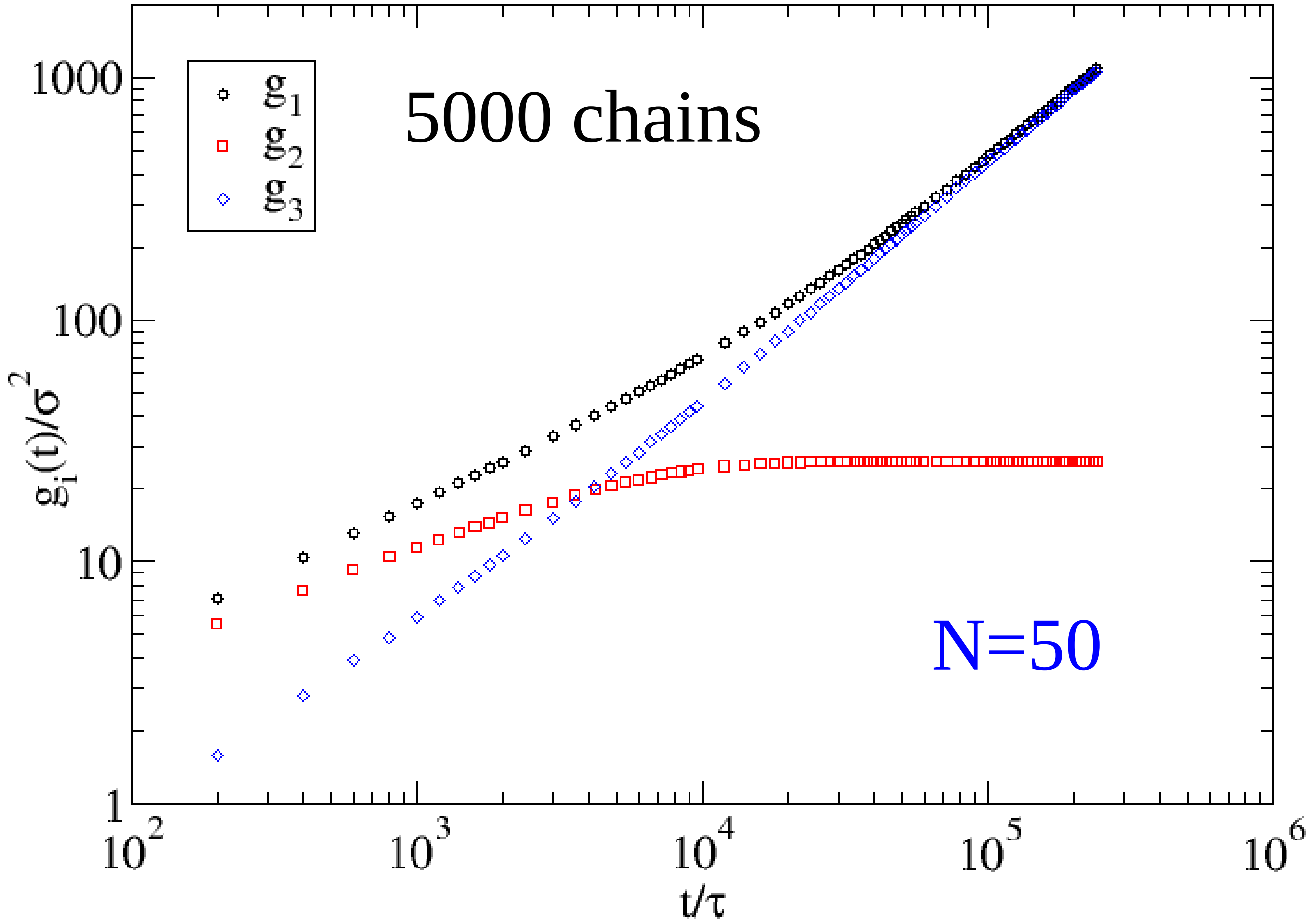
Polymer Chain Confined to Tube

- Coarse grained chain



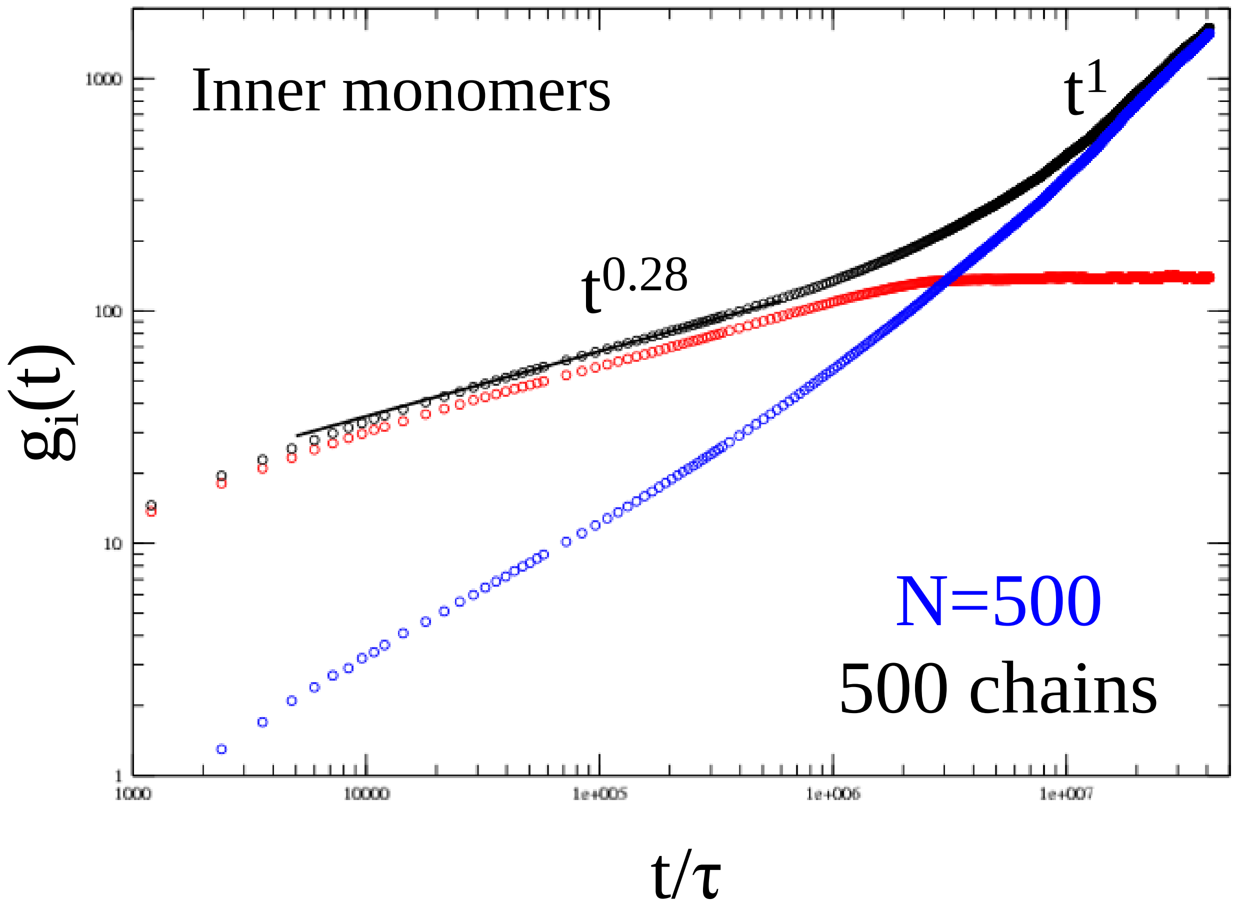
N=400 – 20 plots, 600 τ apart

Motion of Unentangled Polymer



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

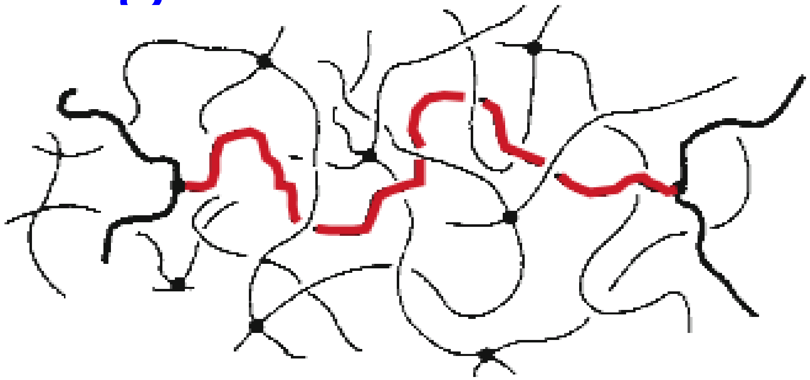
Motion of Entangled Polymer



2 million core hours

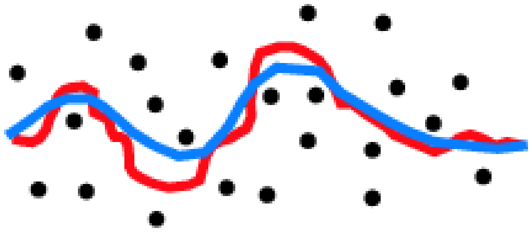
- $t^{1/4}$ motion is clearly seen for inner monomers
- Second $t^{1/2}$ region still unresolved

Topological Approach to Idenify Entanglements

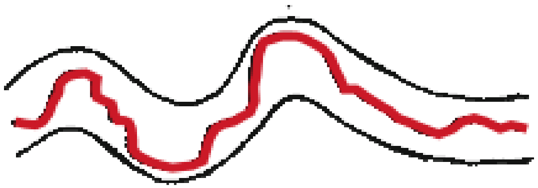


- Microscopic conformation

- Shortest path into which a chain can contract with fixed endpoints and without crossing obstables

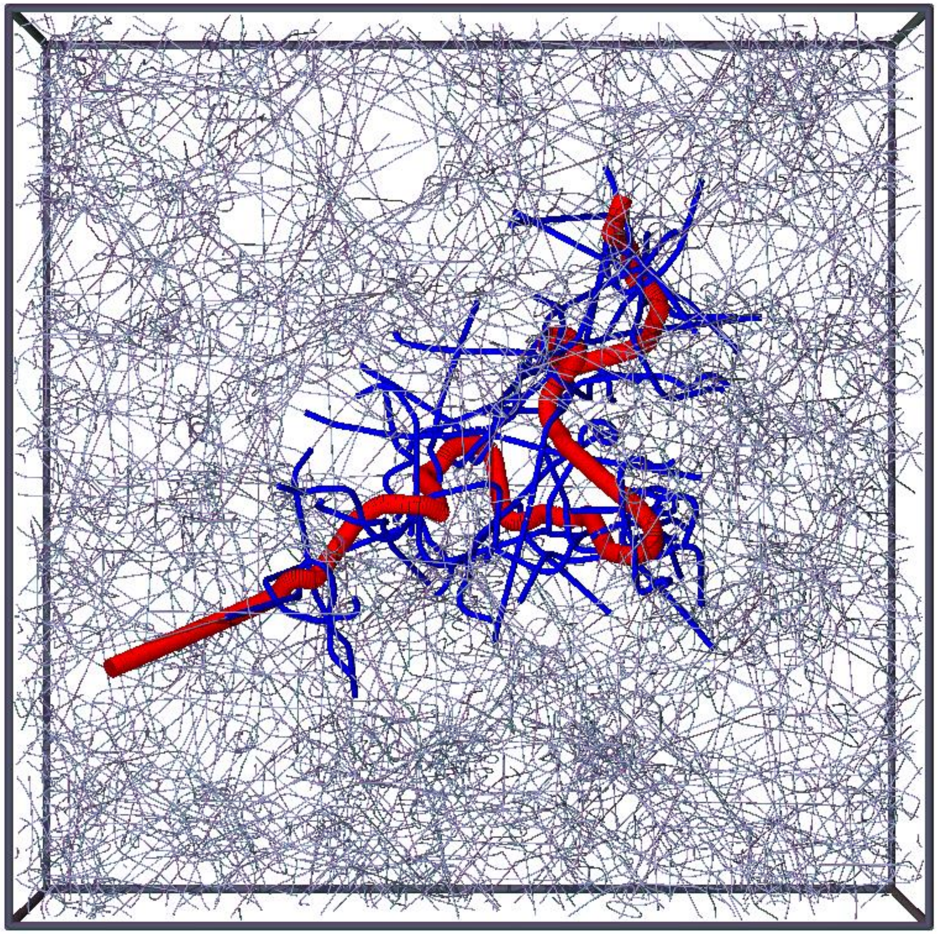


- Tube axis = primitive path



- Need a topological analysis which can follow motion of chain

Primitive Path Analysis



N=700

- Shorter Contour Length

  $L_{pp} = Nb_{pp} < L$
- Larger Kuhn Length

  $a_{pp} > l_k$
- Same spatial extent

  $a_{pp}L_{pp} = R^2 = l_kL$

- Entanglement Length

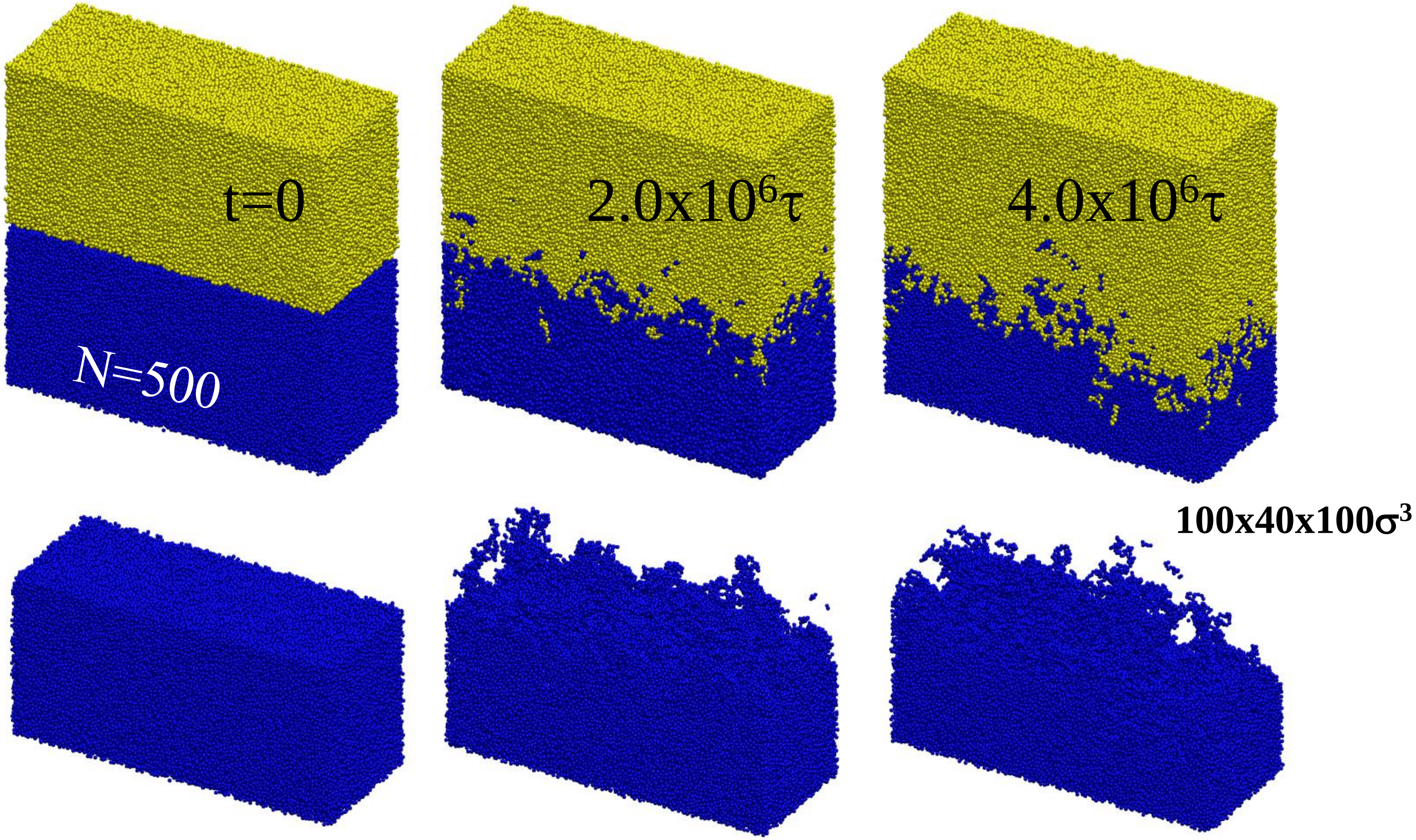
  $N_e = a_{pp}/b_{pp}$
- Packing Length

  $p = 1/\rho_{chain}R^2$

- Primitive paths of a cluster of entangled chains

Self-Healing of Polymer Films

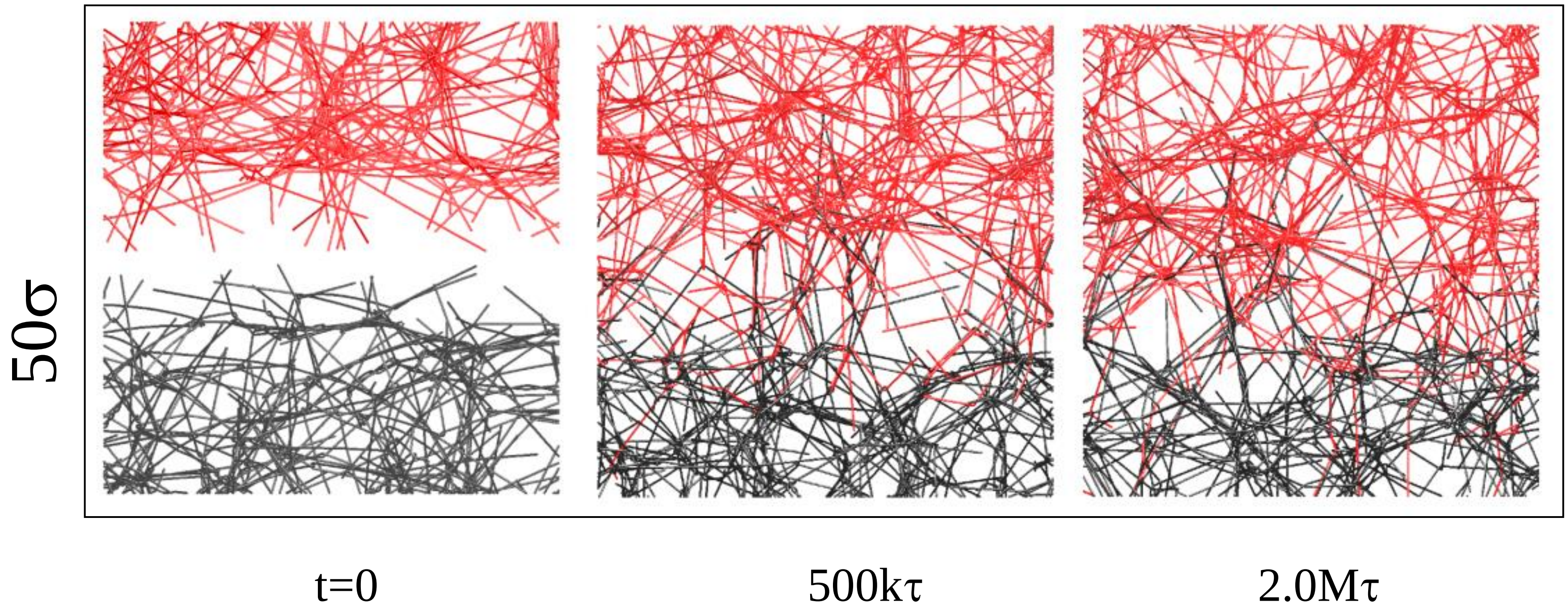
- Development of Entanglements Across an Interface



F. Pierce et al , EPL 95, 46001 (2011)

Entanglements at Interface

- Primitive Path Analysis

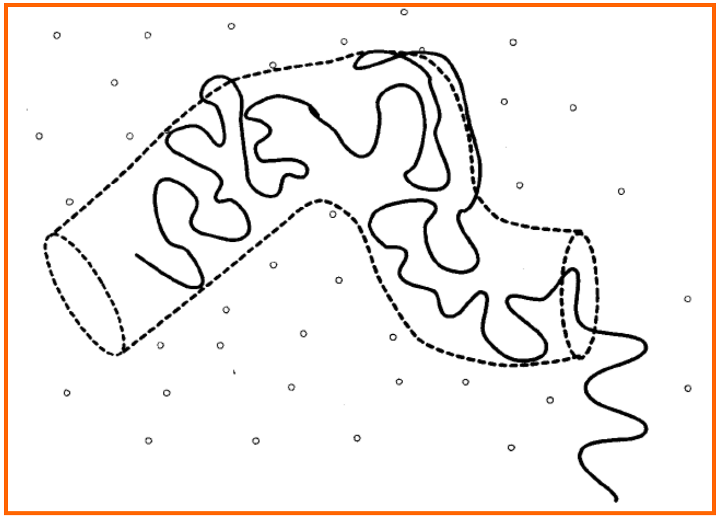


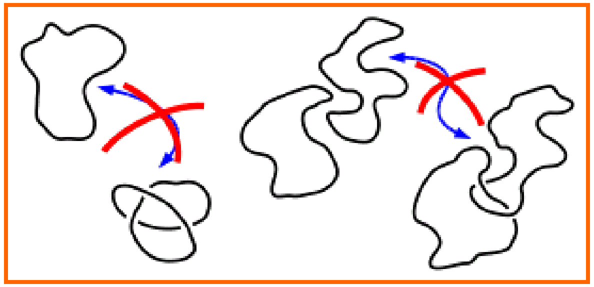
•Interfacial Entanglements form between chains from opposite sides
•Bulk response is fully recovered when the density of entanglements at the interface reaches the bulk value

T. Ge et al, PRE 90, 012602 (2014)

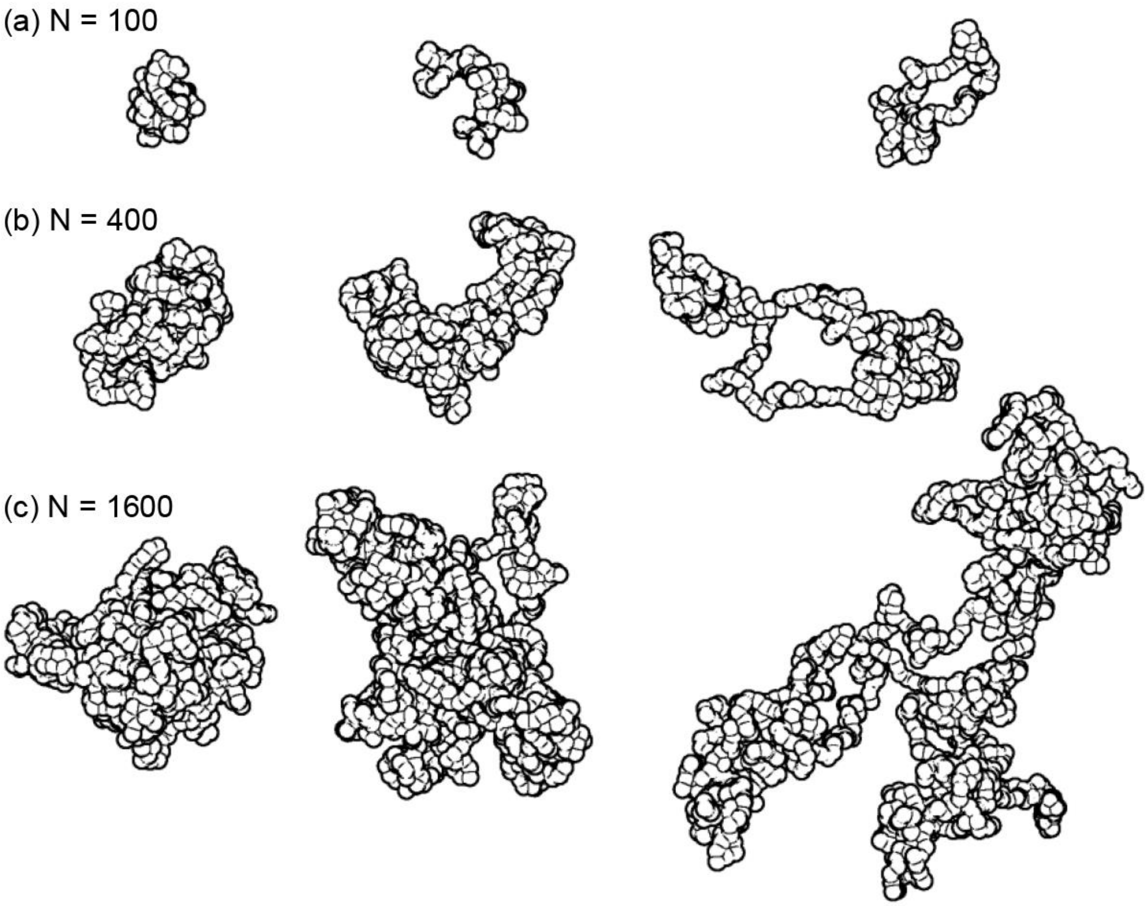
Dynamics of Ring Polymers

- As chain size increases, linear polymers entangle and are forced to move (‘reptate’) along their contours
- Branched polymers relax via a hierarchy of modes from dangling ends moving inward
- Remaining mystery: How do ring polymers relax without beginning or end?





Configurations of Ring Polymers

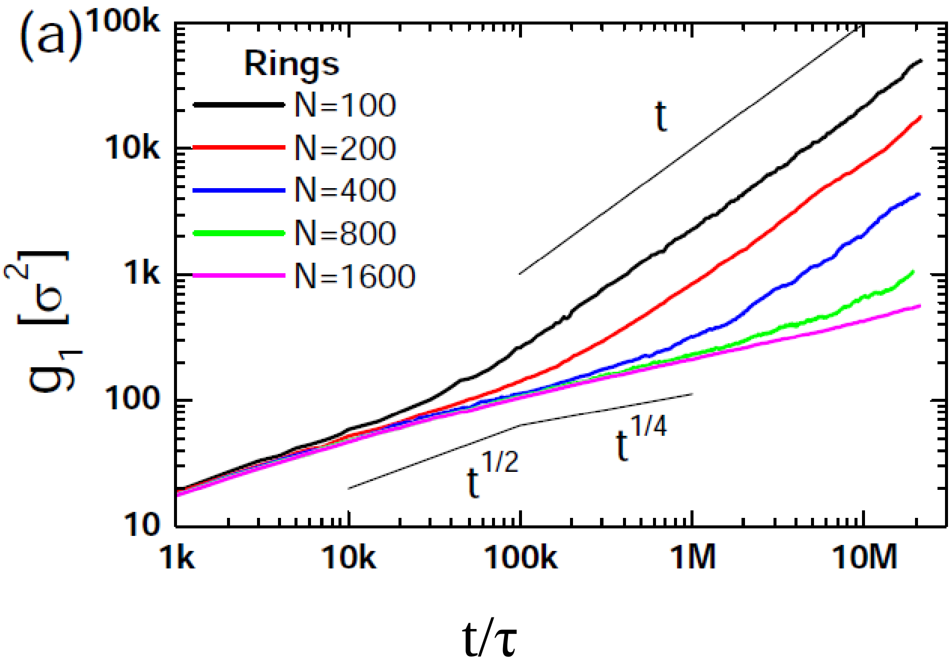


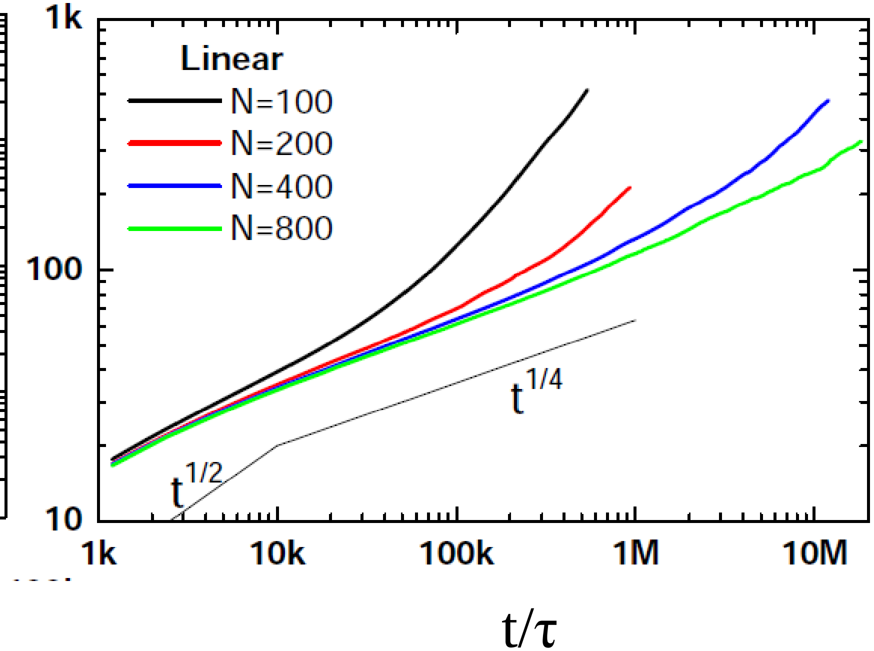
- Rings more compact, less entangled than linear chains
- Radius of Gyration $R_g^2 \sim N^{2/3}$ for rings

  $\sim N$ for linear

J. Halverson et al. J. Chem. Phys. 134, 204904 (2011)

Dynamics of Ring Polymers

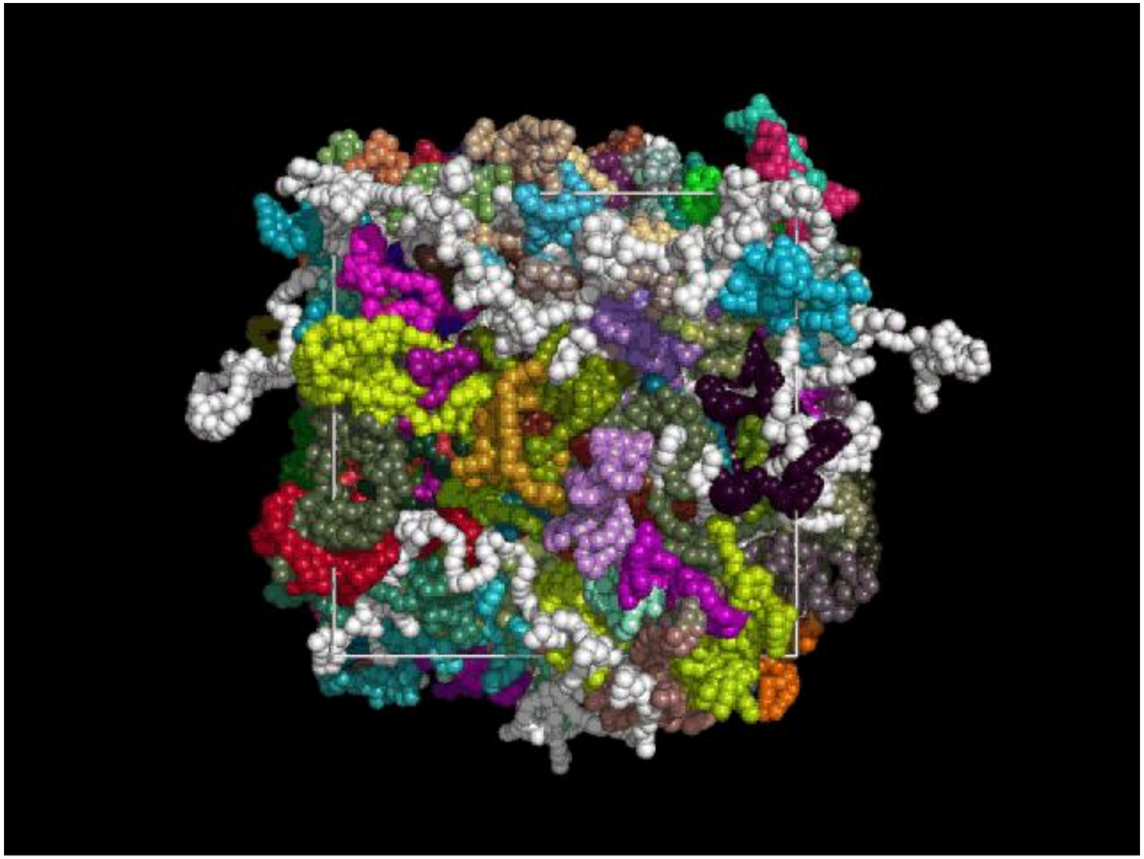




- Ring polymers move much faster than linear chains
- Longest relaxation time $\tau \sim N^2$ for rings, N^3 for linear chains

J. Halverson et al. J. Chem. Phys. 134, 204905 (2011)

Mixture of Ring and Linear Polymers

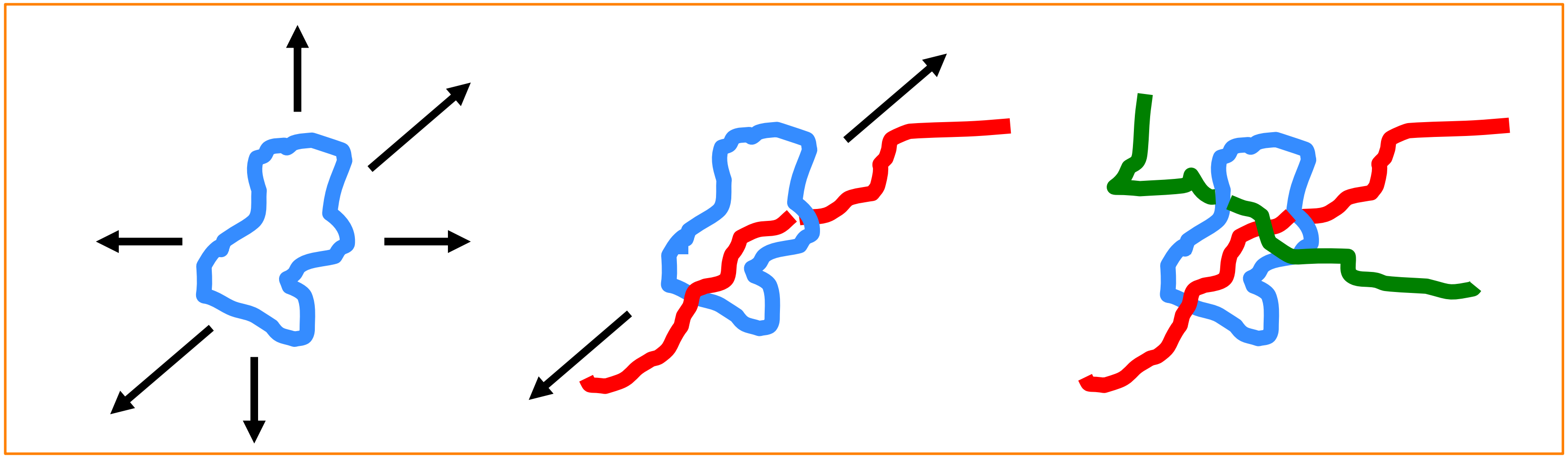


$N = 200,\ M_{\text{rings}} = 200,\ M_{\text{linear}} = 26 \qquad t = 0\ \tau$

J. Halverson et al, PRL108, 038301(2012)

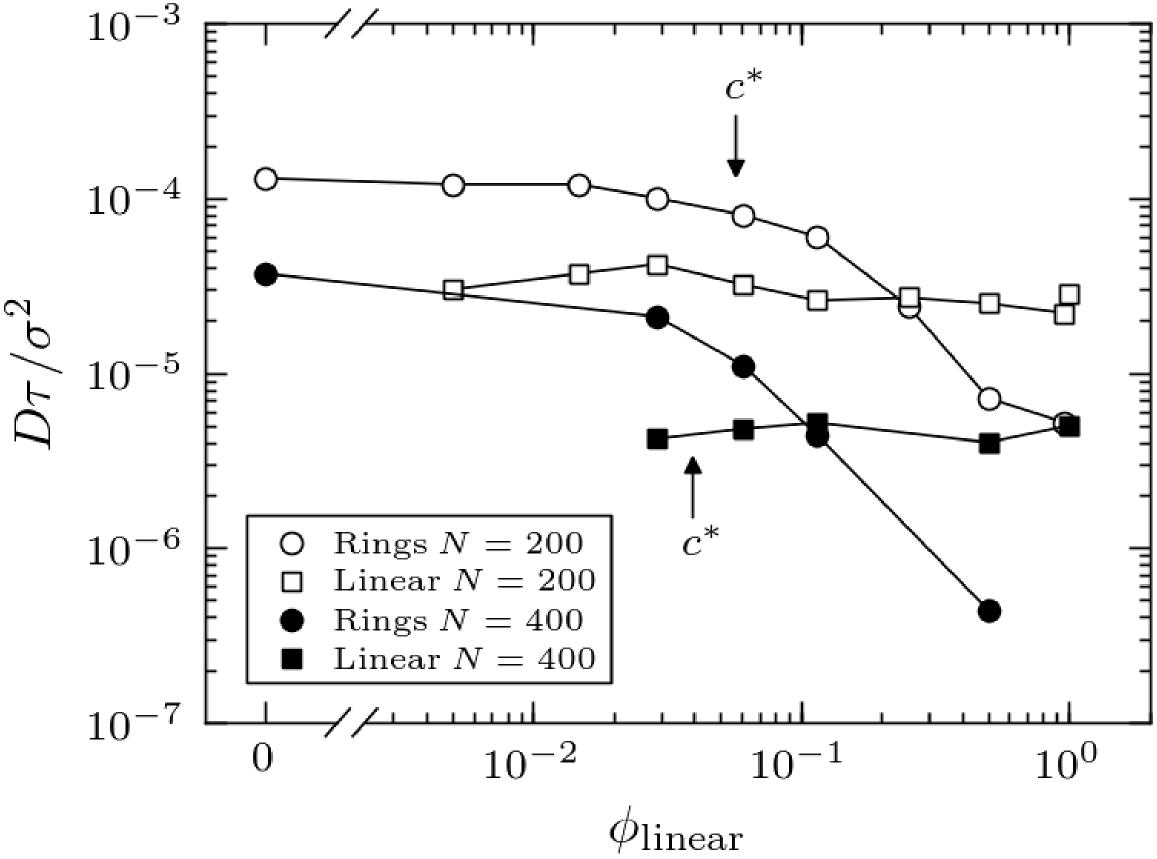
Constrained Motion of Rings in Linear Melt

- Threading causes rings to diffuse more slowly



- Threaded rings can only diffuse along the contour of the linear chain
- Time for constraint release scales as $N^{3.4}$

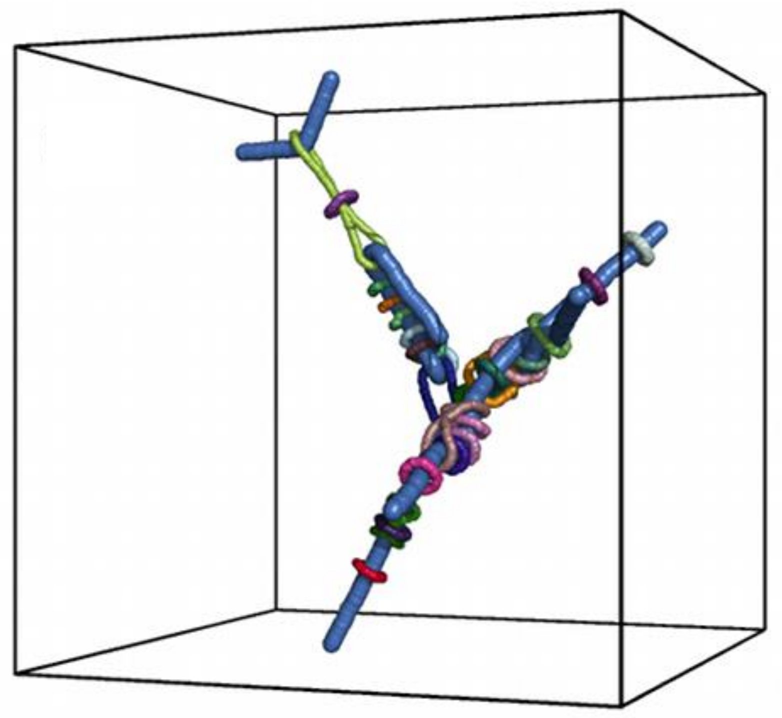
Dynamics of Ring/Linear Blends



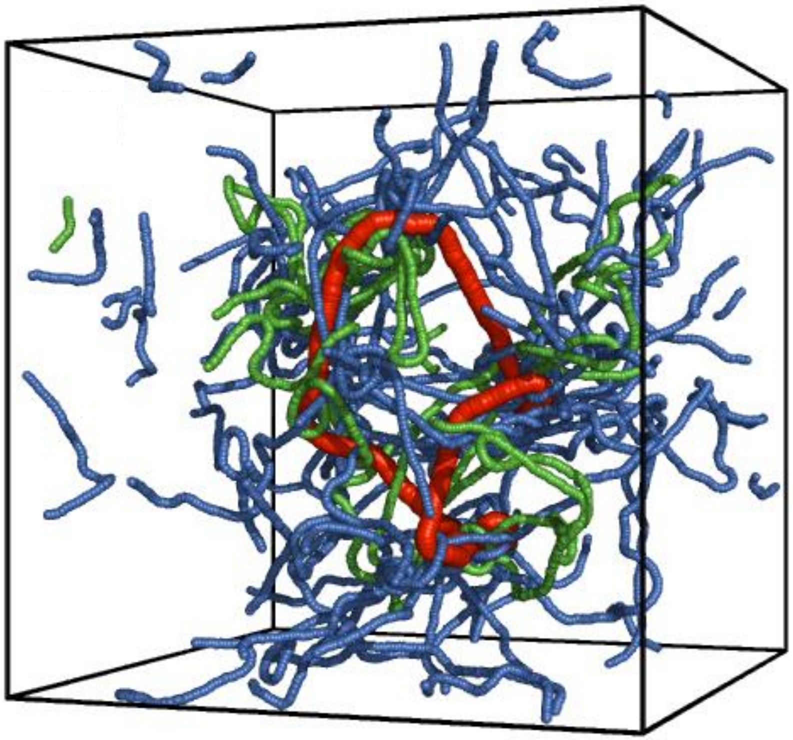
- D_{ring} decreases dramatically when threaded by multiple linear chains (φ_{linear} >0.1)
- D_{linear} is approximately independent of φ_{linear}

Primitive Path Analysis

N=400

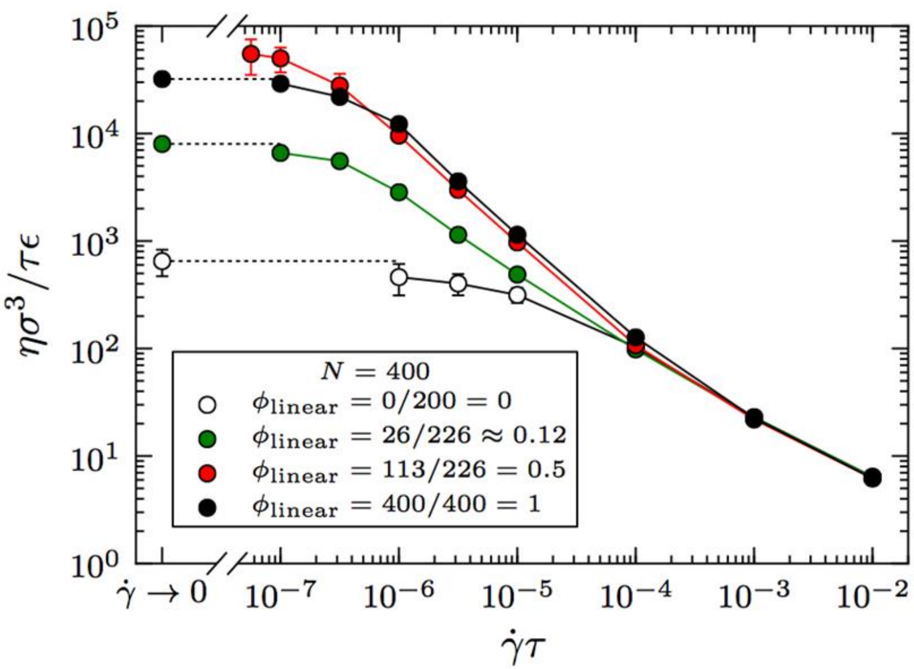


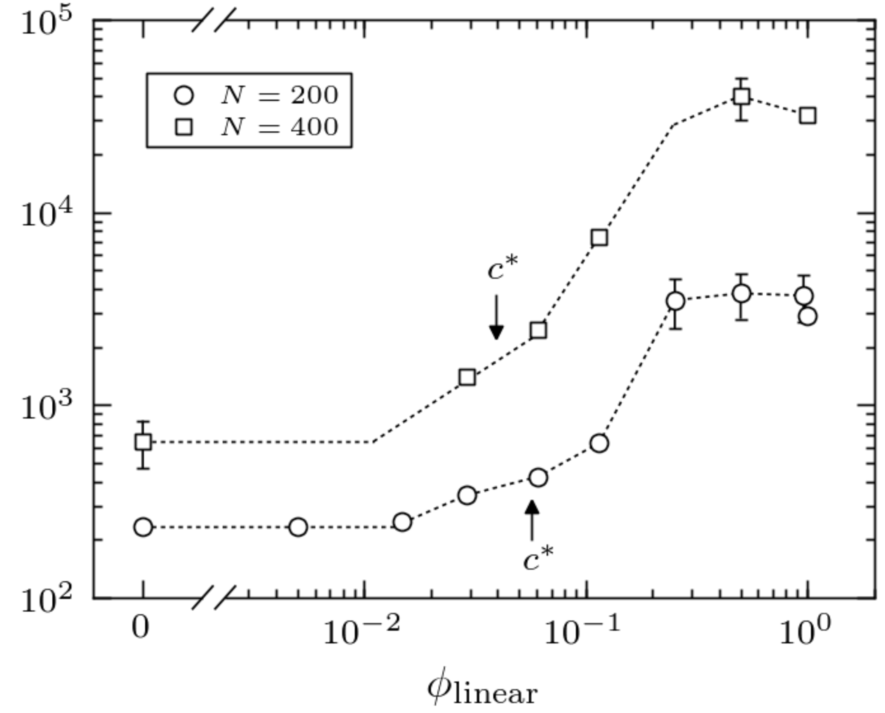
$\phi_{linear} = 3/203 \sim 0.015$



$\phi_{linear} = 113/226 = 0.5$

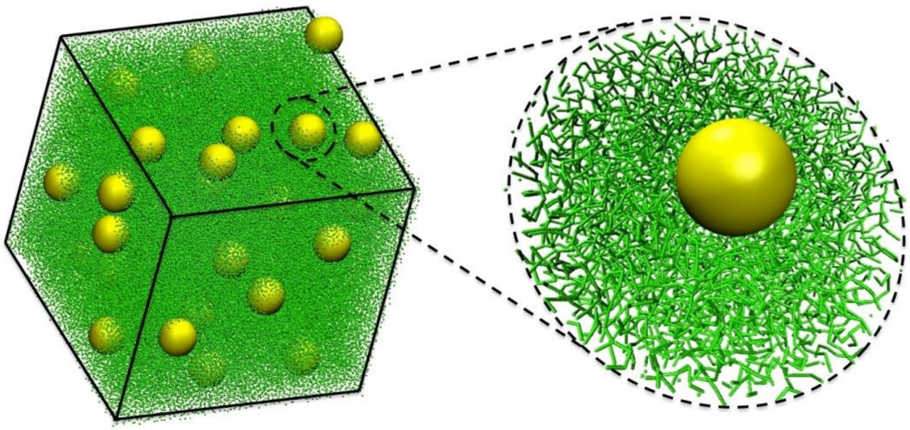
Viscosity of Ring/linear Blends

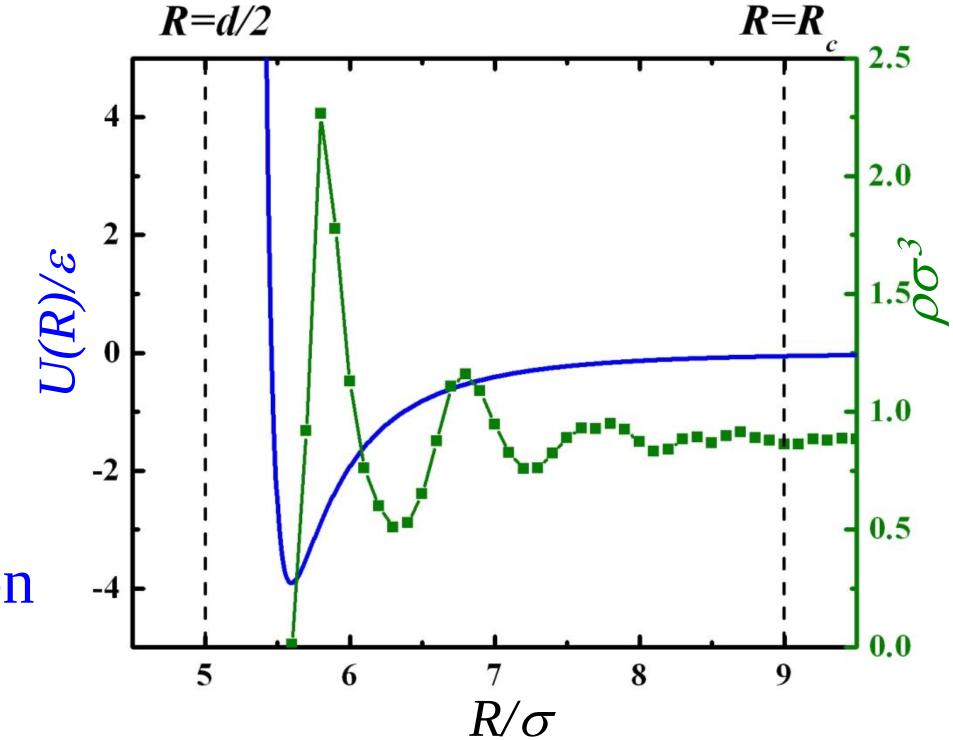




- Onset concentration of $\phi_{\rm linear} \approx 0.01$
- Peak in viscosity for $\phi_{\rm linear} \approx 0.5$

Diffusion of Nanoparticles in Polymers



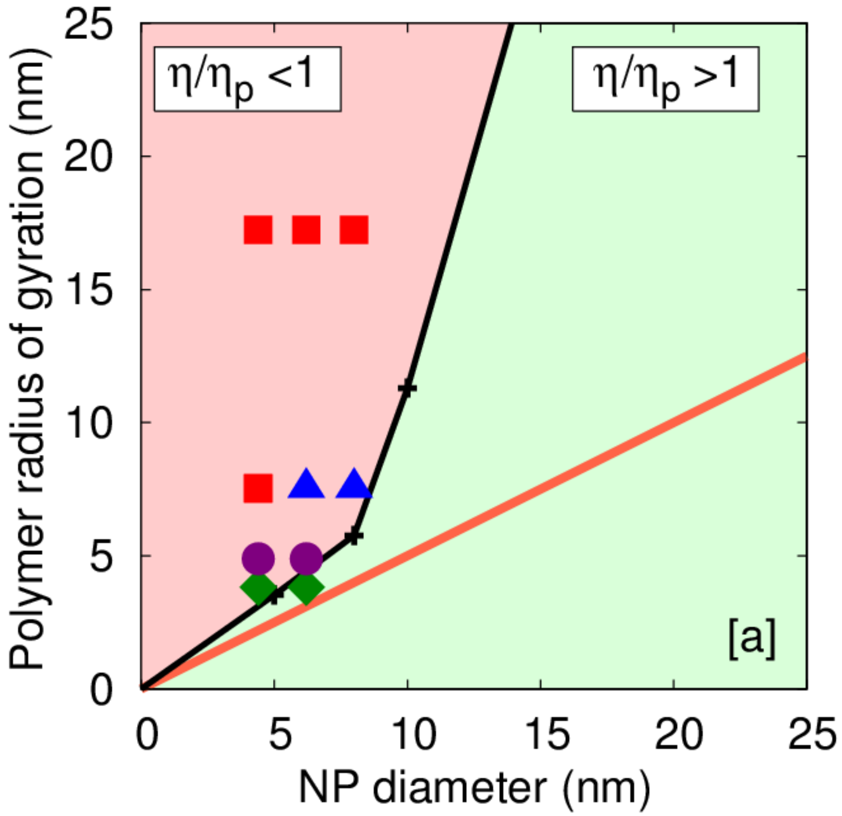


Athermal NP-NP Interaction

Attractive NP-Polymer Interaction for Miscibility

- Weakly interacting mixtures of nanoparticles (NPs) and ring/linear polymers
- NPs of diameter ***d*** are well dispersed at $\varphi_{NP} \sim 0.1$

Viscosity of Polymer Nanocomposites

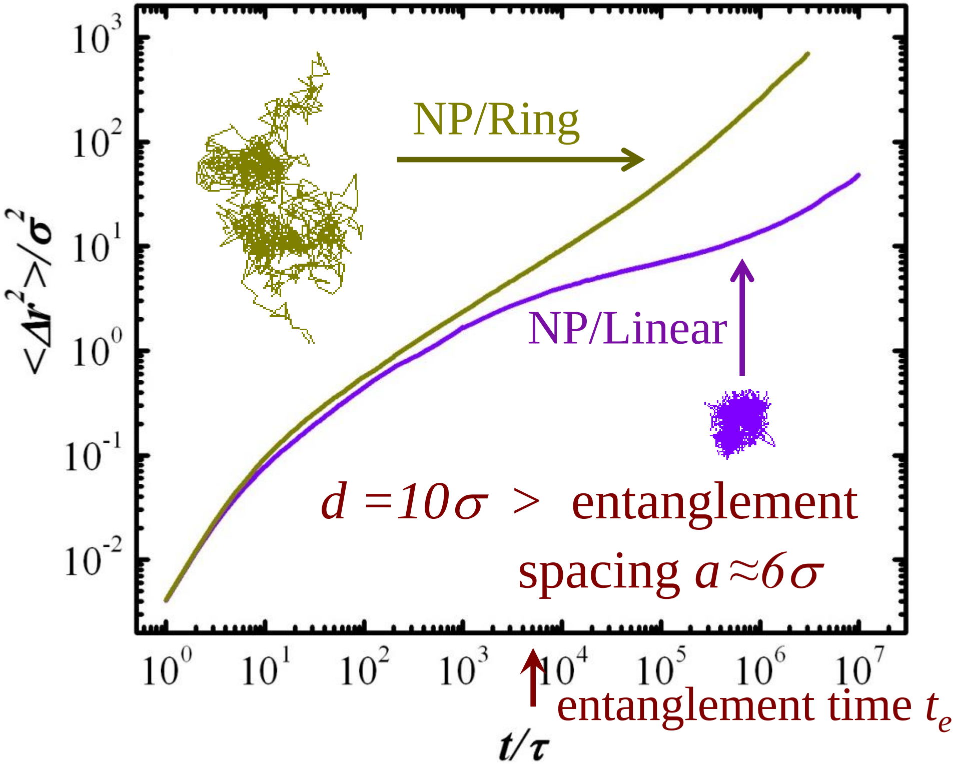


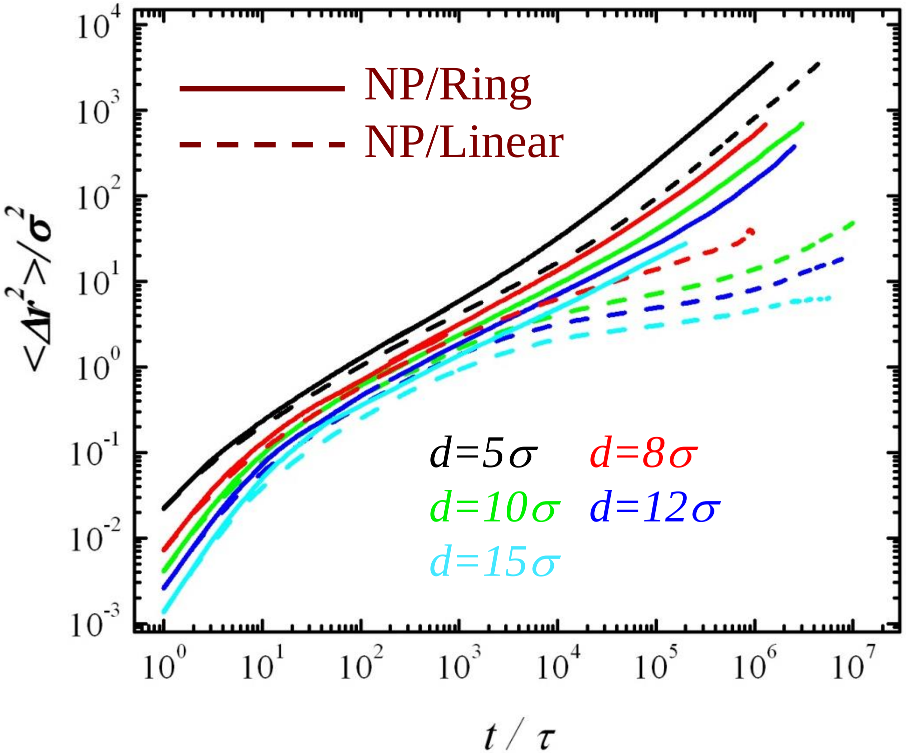
- Small, neutral NPs act akin to plasticizers
  - -reduce the viscosity of polymer melt
- Effect persists for particles whose sizes are as large as chain size or entanglement mesh size
- Overcome by making the chain-NP interactions significantly attractive

A. Tuteja et al., Macromolecules 38, 8000 (2005)

J. Kalathi, PRL 109, 198301 (2012)

Mean-Squared Displacement of NPs

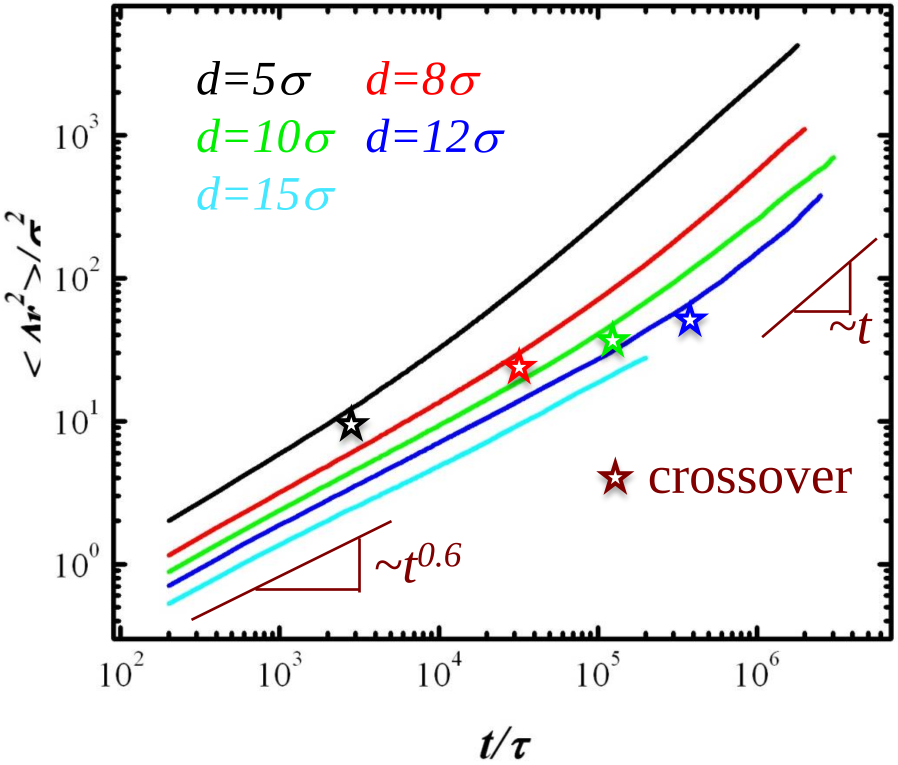


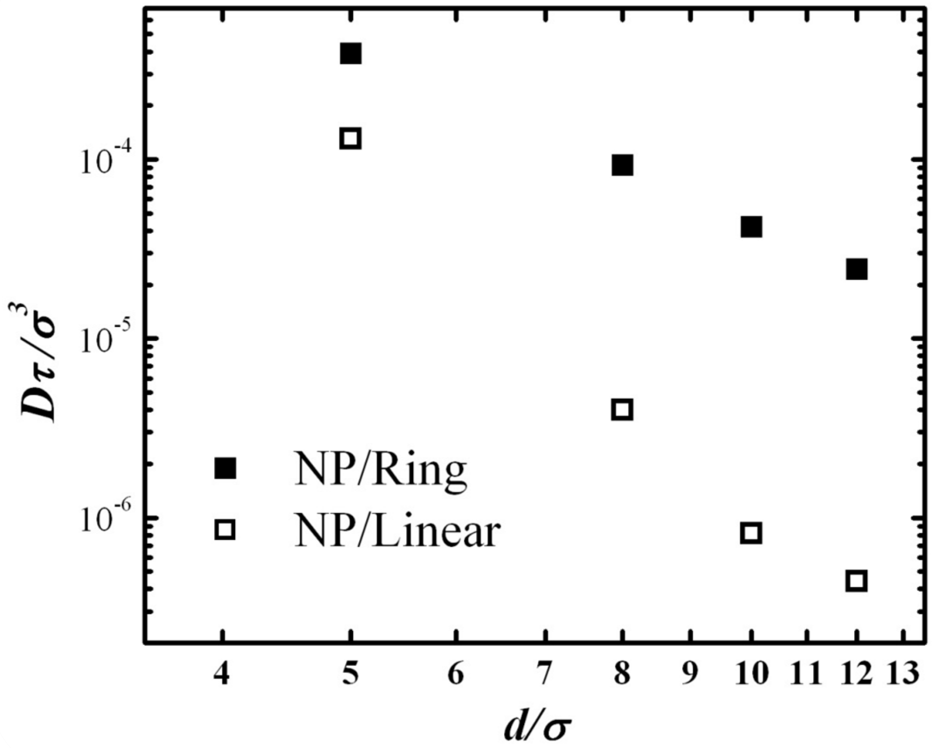


- $t_0 < t < t_e$, sub-diffusive motion due to coupling with dynamics of the subsections of polymer chains
- $t > t_e$, before Fickian diffusion, motion of NPs with $d > a$
  - Trapped by the entanglement mesh in linear polymers
  - Remains subdiffusive in rings, no entanglement mesh

T. Ge et al, in prep (2015)

Fickian Diffusion of Nanoparticles





- Crossover occurs as NP motion couples with coherent motion of chain subsections of size $R_g \sim d$
- Rings: $D \sim d^{-3.2}$, theory predicts $D \sim d^{-4.5}$
- Linear: $D \sim d^{-4.5}$, theory predicts d^{-3}
- Crossover to Stokes-Einstein $d > 20\sigma$

Highlights

- Simulations identified for the first time the reptation motion of polymers

- Followed entanglements of polymer using Primitive Path Analysis to predict macroscopic properties

- Ring polymers move much faster than linear chains
  - Relaxation time ~ N^2 for rings

- Threading causes rings to diffuse very slowly in ring/linear mixtures

- Small nanoparticles act as diluent, decrease viscosity

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, ….

Acknowledgements

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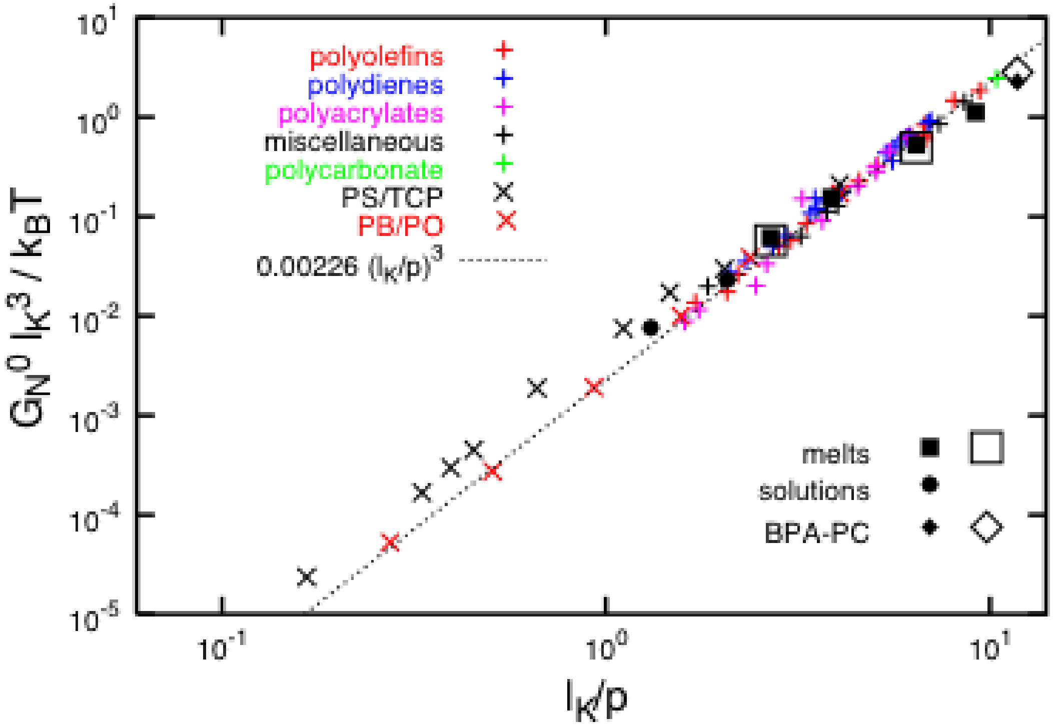
Computer Resources:

- Advanced Scientific Computing Research (ASCR) Leadership Computing Challenge (ALCC) at the National Energy Research Scientific Computing Center (NERSC)
- Sandia National Laboratories

Predicting the Plateau Modulus from PPA



$$G_N^0 = 0.00226 k_B T/p^3$$

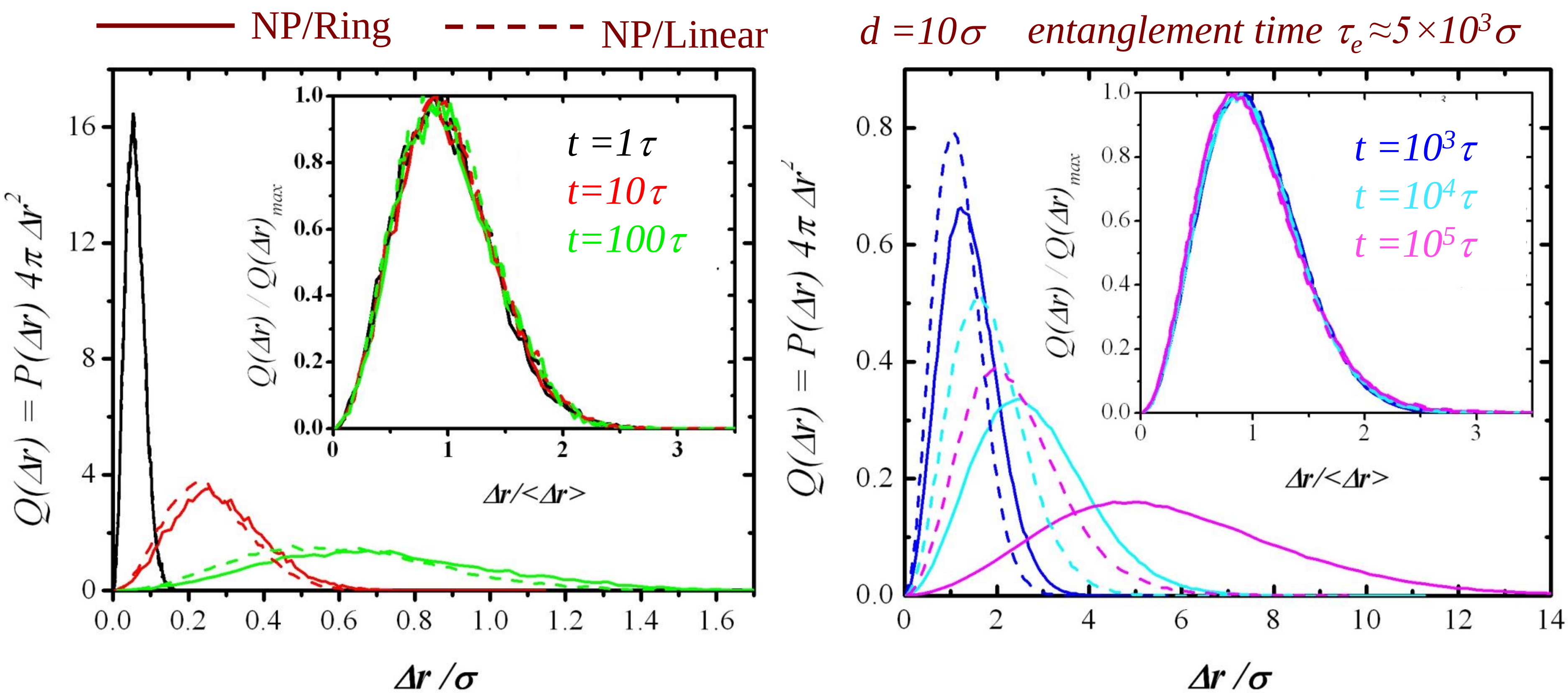
L. Fetters *et al.*, J. Polym. Sci B: Polym. Phys. 37, 1023 (1999)

$$G_N^0 = \frac{4}{5}\frac{k_B T}{a_{pp}^2 p}$$

- Parameter free prediction for plateau modulus

Extended to solutions of semi-flexible polymers –
N. Uchida *et al.*, JCP 128, 044902 (2008)

Probability Distribution of NP Displacement



- Nearly Gaussian distribution of NP displacement
- Entanglement mesh reduces the mean displacement for linear chians but does not change the distribution
- No evidence of NP hopping