

# Entanglement in solutions of semiflexible polymers

# Outline

1. Overview of entanglement phenomena
2. Brownian dynamics simulations of entangled solutions

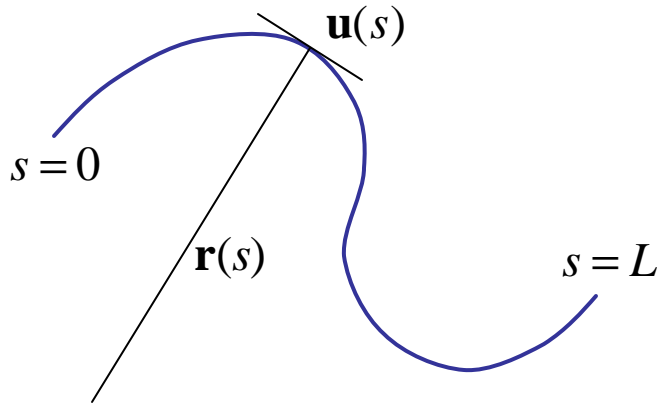
Shriram Ramanathan

3. A statistical mechanical theory for the tube diameter

D.M., Phys. Rev. E 63, 031502 (2002)

Funding: NSF-DMR, ACS-PRF

# Wormlike Chains



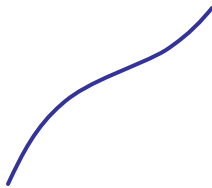
bending energy

$$U = \frac{1}{2} \mathbf{k} \int_0^L ds \left| \frac{d\mathbf{u}(s)}{ds} \right|^2$$

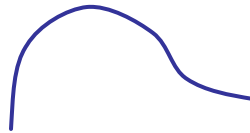
persistence length:

$$L_p \equiv \frac{\mathbf{k}}{\mathbf{k}T}$$

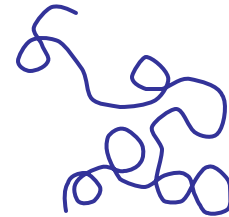
$$\langle \mathbf{u}(s) \cdot \mathbf{u}(s') \rangle_{eq} = e^{-|s-s'|/L_p}$$



$$L \ll L_p$$



$$L \approx L_p$$



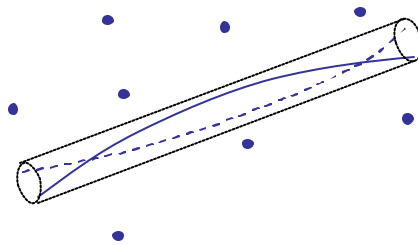
$$L \gg L_p$$

# Concentration Regimes - Semiflexible Rods ( $L < L_p$ )

Dilute  
 $c < c^*$

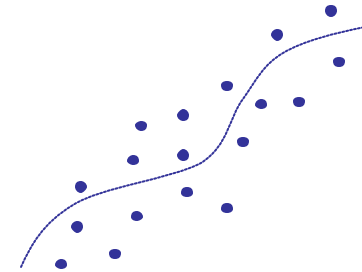


“Loosely” entangled  
 $c^* < c < c^{**}$



hindered rotation  
 free bending

“Tightly” entangled  
 $c > c^{**}$



hindered rotation  
 hindered bending

$$c^* \approx \frac{1}{L^3}$$

$$c^{**} \approx c^* \sqrt{\frac{L_p}{L}}$$

Notation:  $c = \# \text{ chains} / \text{volume}$

$\rho = cL = \text{chain length} / \text{volume}$

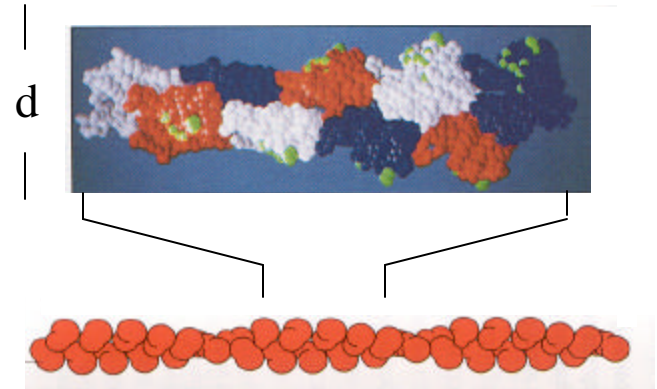
# Solutions of Actin Protein Filaments

- Filament:

$$d \approx 8\text{nm} = 0.008 \text{ } \mu\text{m}$$

$$L = 1 - 30 \text{ } \mu\text{m}$$

$$L_p = 17 \pm 1 \text{ } \mu\text{m}$$



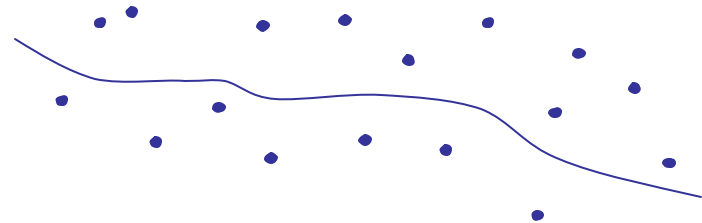
- Concentration:

$$c = 0.1 - 1 \text{ mg/ml} = 0.01 - 0.1 \%$$

$$r \equiv \frac{\text{filament length}}{\text{volume}} \approx 4 - 40 \text{ } \mu\text{m}^{-2}$$

$$L_m \equiv r^{-1/2} \approx 0.51 - 0.16 \text{ } \mu\text{m}$$

$$\frac{L_m}{L} = \text{mesh size}$$

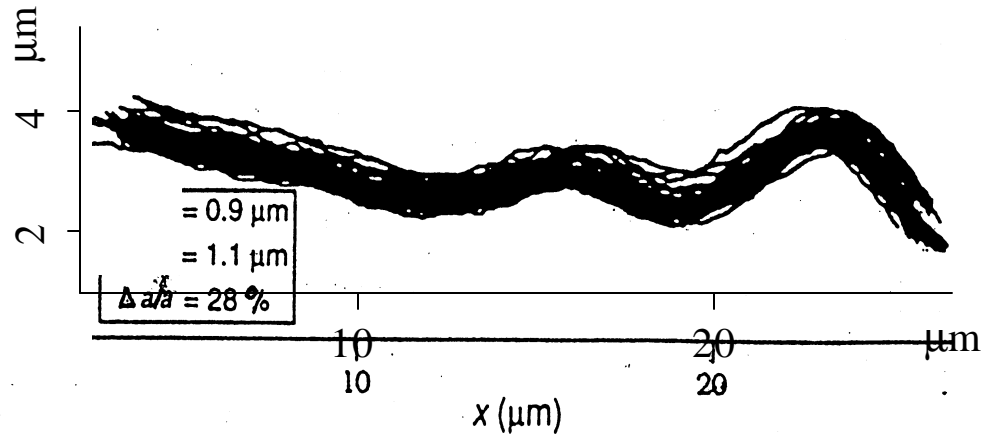


- Hierarchy:  $d \ll L_m \ll L \approx L_p$

# Flourescence Microscopy of Entangled Actin Filaments

J. Käs *et al.*, *Nature* (1994); *Biophysical J.* (1996).

- Technique: Flourescently label a small fraction of filaments in an entangled solution. Overlay chain contours from 60 micrographs taken at 0.1 sec intervals



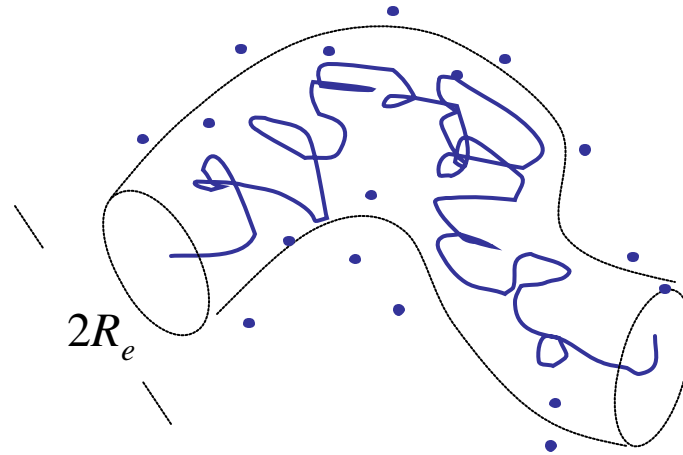
- Conditions: 0.1 mg Actin / ml water  $L_m = 1/\sqrt{r} \approx 0.51 \text{ } \mu\text{m}$
- The polymer rapidly explores a tubelike region of topologically accessible contours.
- Over much longer times, reptation can be observed

# Concentration Regimes - Semiflexible Coils ( $L \gg L_p$ )

Dilute  
 $c < c^*$



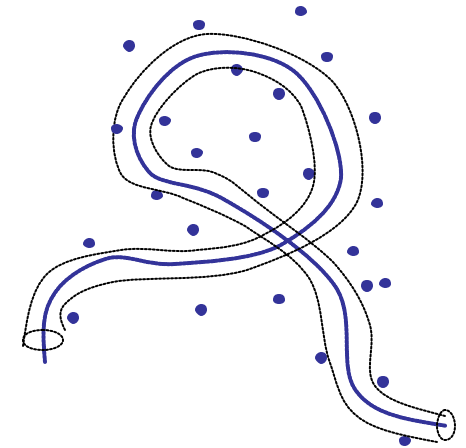
“Loosely” entangled  
 $c^* < c < c^{**}$



$$L_e, R_e \gg L_p$$

$$L_m \gg L_p$$

“Tightly” entangled  
 $c^{**} < c$



$$L_e, R_e \ll L_p$$

$$r^{**} \approx \frac{1}{L_p^2}$$

$L_e$  = entanglement contour length

$R_e$  = tube radius

# Isotropic Nematic Transition

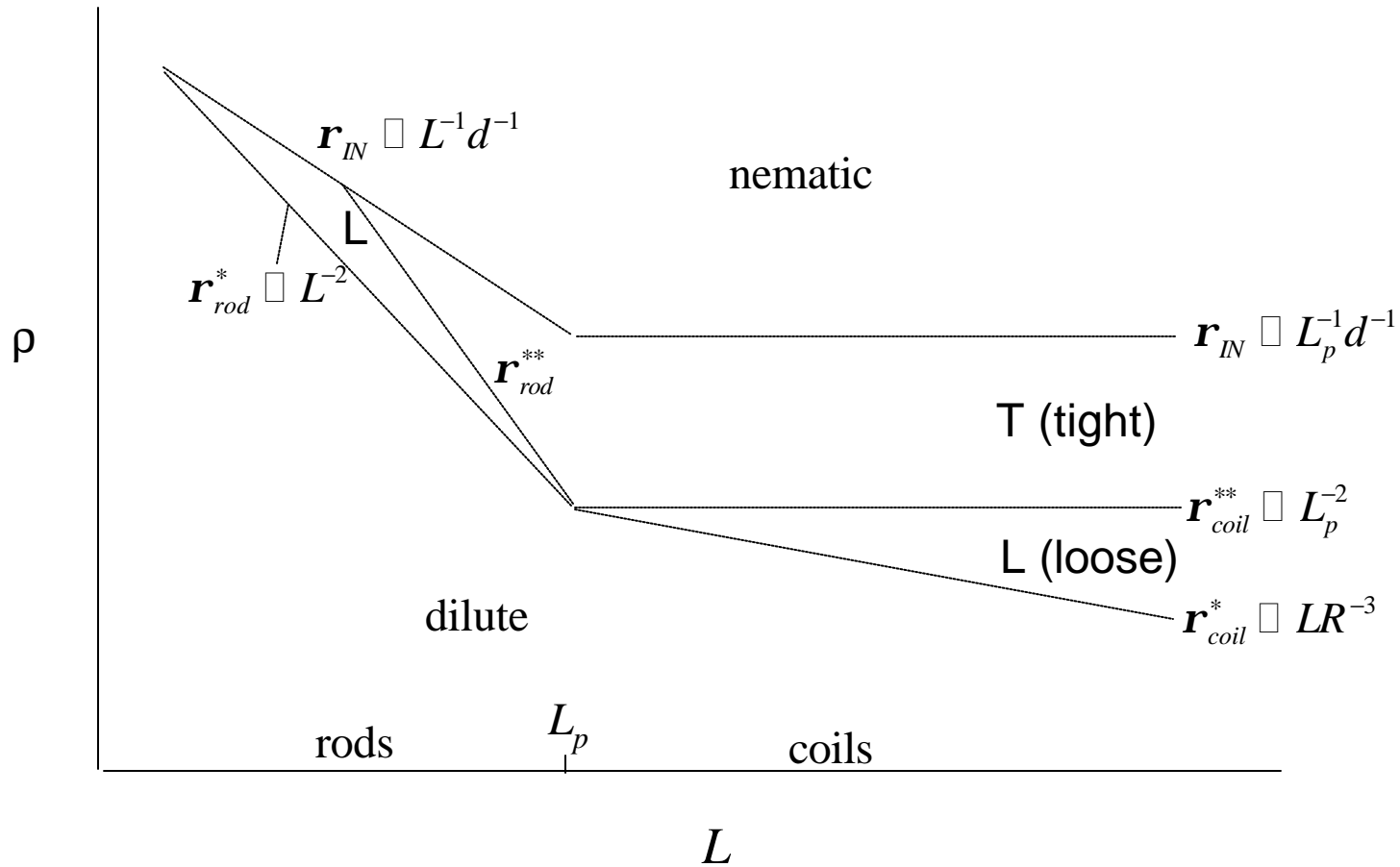
- Transition driven by excluded volume, and so depends on diameter  $d$
- For rigid rods ( Onsager )

$$\mathbf{r}_{IN} \propto \frac{5}{Ld} \qquad c_{IN} \propto \frac{5}{L^2d}$$

- For semiflexible coils (  $L \gg L_p$  ) (Khokhlov and Semenov)

$$\mathbf{r}_{IN} \propto \frac{7}{L_p d}$$

# Concentration Regimes



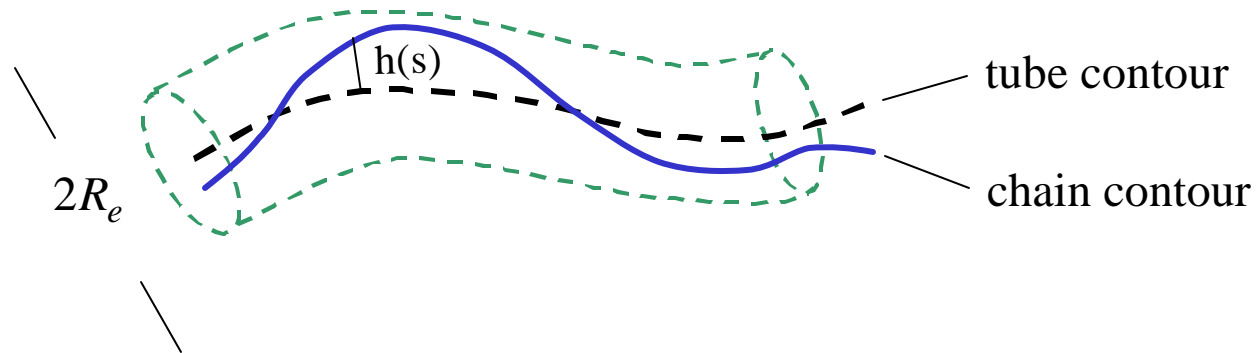
•Width of tightly entangled regime  $\frac{\rho_{IN}}{\rho_{rod}^{**}} \leq \frac{L_p}{d}$

## Model "Rodlike" Polymers

	$d$	$L_p$	$L$	$L_p/d$	wt %	$\mathbf{r}L_p^2$
PLBG poly(benzyl glutamate)	1.5 nm	150 nm	40 – 200 nm	100	< 10	< 1000
FD virus	7 nm	2.2 $\mu\text{m}$	0.9 $\mu\text{m}$	300	< 2	< 2000
F-actin	8 nm	17 $\mu\text{m}$	1 – 20 $\mu\text{m}$	2000	< 0.2	< 20,000

- The most heavily studied “rod like” polymers all have  $L / L_p = 0.5 - 1.0$
- F-actin has been studied as a model polymer from 1990 – present. Fluorescence microscopy and rheological data show clear evidence of tight entanglement.
- PBLG was studied as a rodlike polymer in 1980s. Data for viscosity and rotational diffusivity were interpreted in terms of Doi-Edwards rigid rod model. Is tight-entanglement relevant?

# Semiflexible Polymer in a Tube



- Fluctuations [  $h(q)$  = Fourier amplitude ]

$$\langle |h(q)| \rangle^2 = \frac{kT}{kq^4 + g(q)}$$

- Entanglement wavenumber / length

$$kq_e^4 \approx g(q_e)$$

$$L_e \approx q_e^{-1}$$

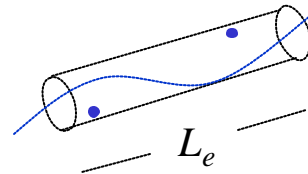
- Relationship of  $R_e$  and  $L_e$  (Odijk)

$$R_e^2 \equiv \langle h^2(s) \rangle = \int \frac{dq}{2p} \frac{kT}{kq^4 + g(q)} \approx \int_{1/L_e} \frac{dq}{2p} \frac{kT}{kq^4} \approx \frac{L_e^3}{L_p}$$

$$R_e \approx L_e^{3/2} L_p^{-1/2}$$

- Assume that  $O(1)$  other chains pierce the tube per entanglement length (Semenov)

$$1 \approx r R_e L_e$$



- Combining  $L_e \approx R_e^{2/3} L_p^{1/3} \approx r^{-1} R_e^{-1}$

$$R_e \approx r^{-3/5} L_p^{-1/5}$$

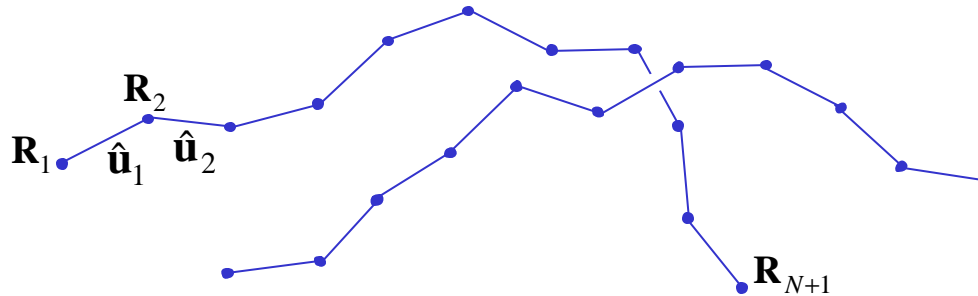
$$L_e \approx r^{-2/5} L_p^{1/5}$$

$$\approx L_p (r L_p^2)^{-3/5}$$

$$\approx L_p (r L_p^2)^{-3/5}$$

# Brownian Dynamics Simulations of Entangled Solutions

- Stochastic simulations of wormlike bead-rod chains, with constrained rod lengths



$$\mathbf{v} \frac{d\mathbf{R}_i}{dt} = -\frac{\partial U_{bend}}{\partial \mathbf{R}_i} + \underbrace{\hat{\mathbf{u}}_i l_i - \hat{\mathbf{u}}_{i-1} l_{i-1}}_{\text{constraint}} + \underbrace{?}_i_{\text{random}}$$

- Topological constraints imposed by rejection of moves that cause chain intersections (infinitely thin uncrossable chains)

- Initial conformations constructed with thermal equilibrium distribution

- Conditions:  $L = 0.5 L_p - L_p$        $N = 10 - 40$        $cL^3 = 0 - 4000$

- For comparison, also conducted "slithering snake" simulations of pure reptation

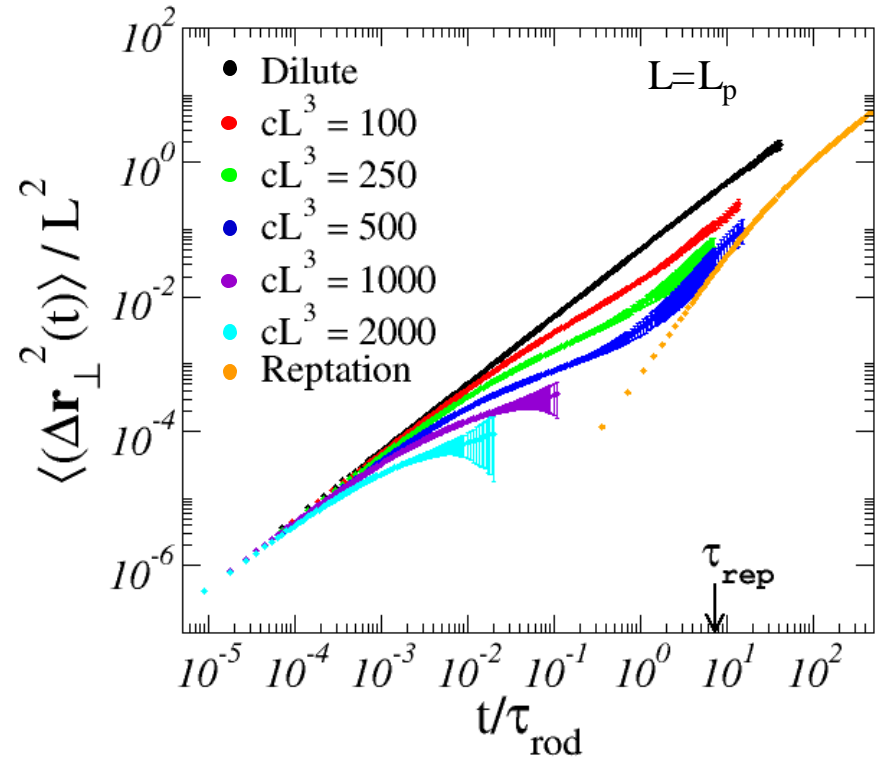
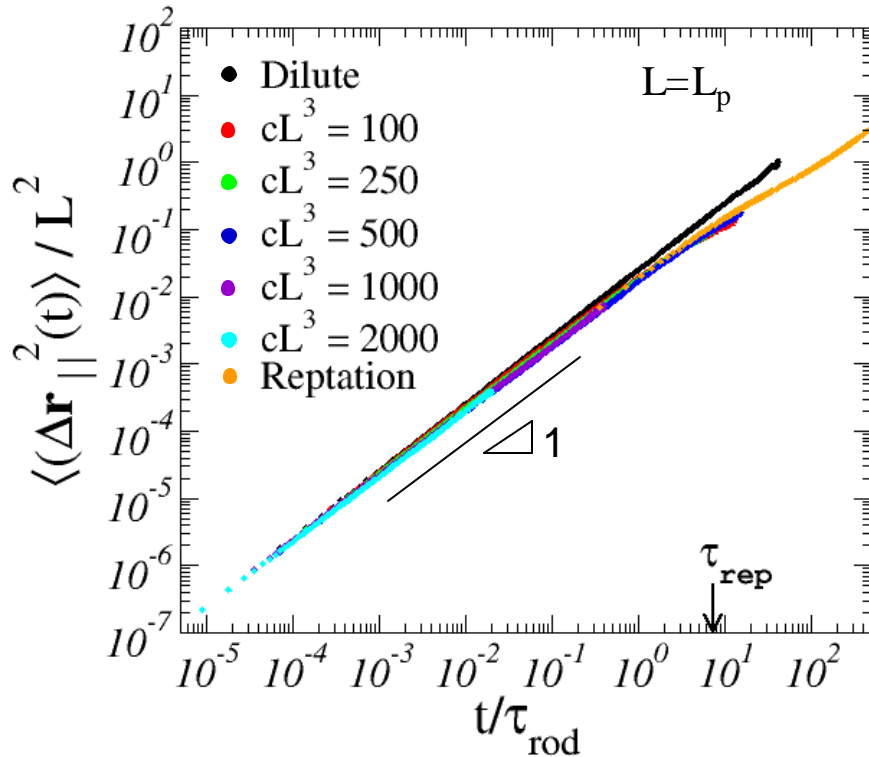
# Mean square displacement (MSD) of center of mass (COM)



$\tau_{\text{rod}}$  = rod rotation time in dilute solution  
 $\tau_{\text{rep}}$  = reptation time

Parallel

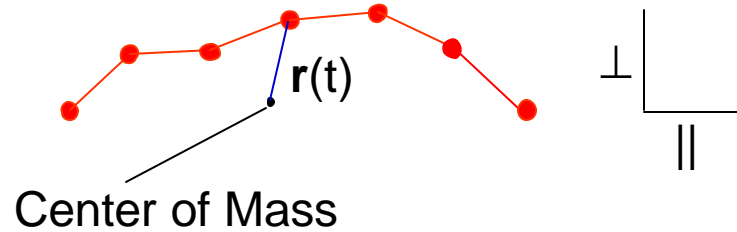
Transverse



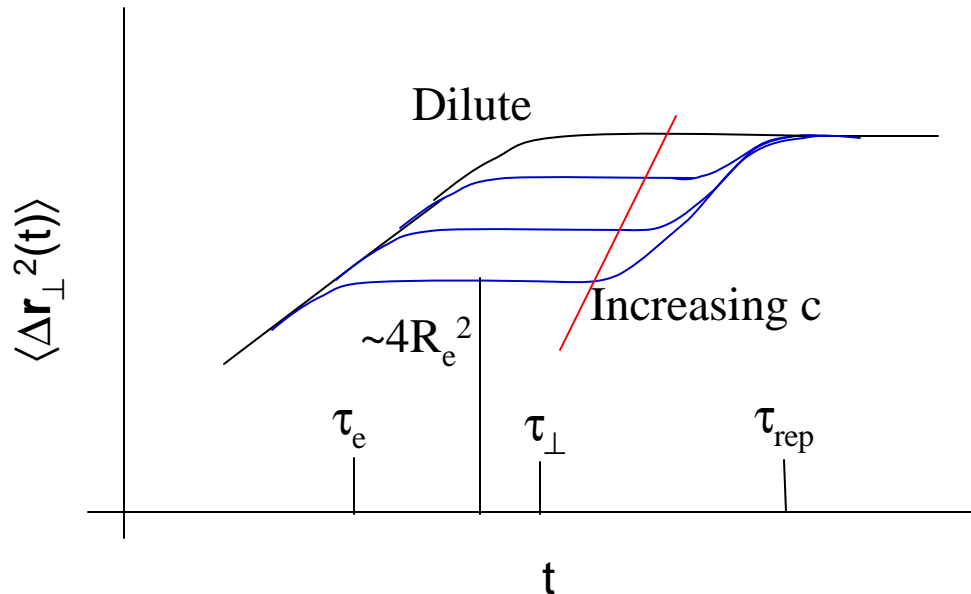
- Transverse motion of COM is suppressed, while longitudinal diffusion is unaffected
- Transverse COM motion matches reptation simulation for  $cL^3 = 500$  at large  $t$

# MSD of middle bead in a center of mass reference frame

- Transverse motion of the middle bead relative to the COM reflects the bending motion of the chain. Note that  $\mathbf{r}(t) = 0$  for a rigid rod



- Expected Behavior:

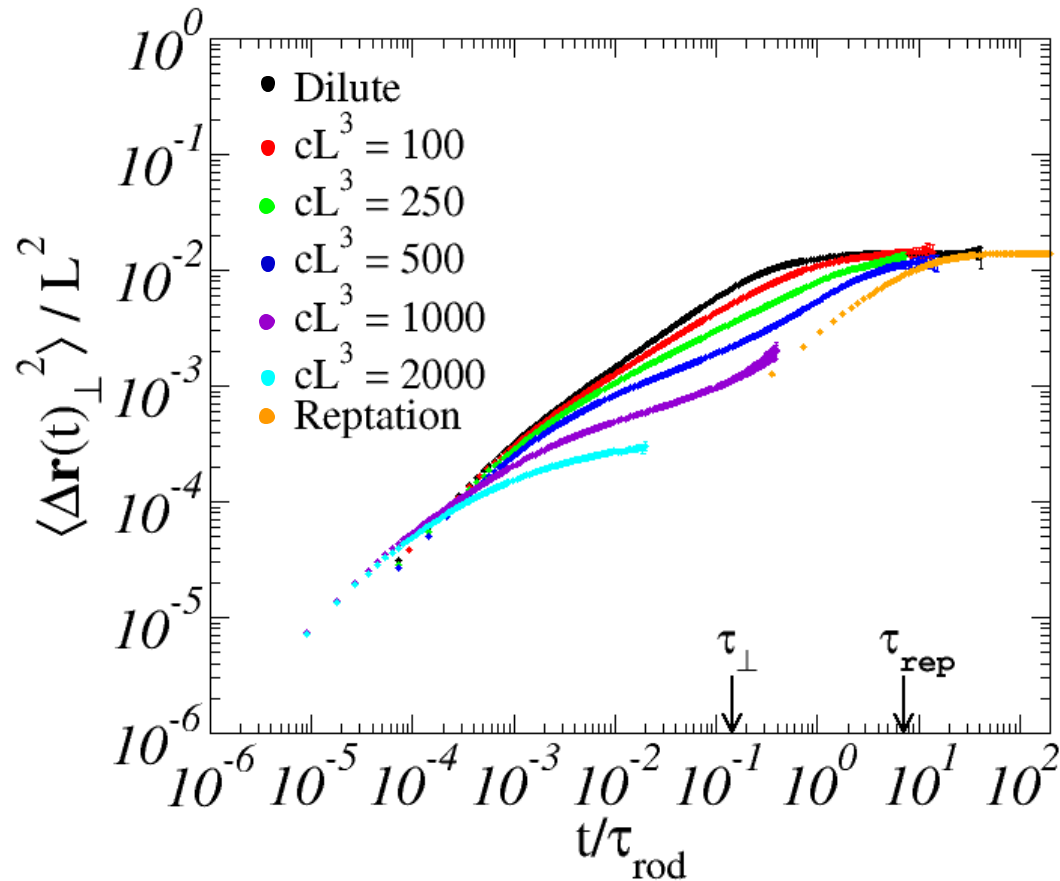


$\tau_\perp$  = relaxation time of slowest bending mode in dilute solution

$\tau_e$  = entanglement time

$R_e$  = tube radius

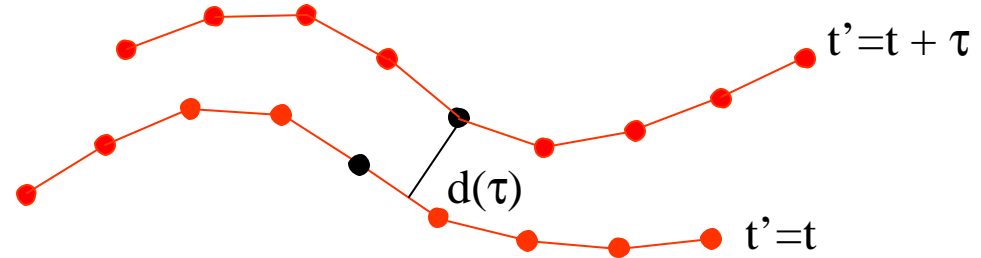
# Transverse MSD of middle bead in COM frame ( $L=L_p$ )



- For  $cL^3=1000$ , MSD approaches reptation simulation beyond the plateau
- For  $cL^3 = 500$ , MSD approaches dilute solution value at  $\tau_{\text{rep}}$

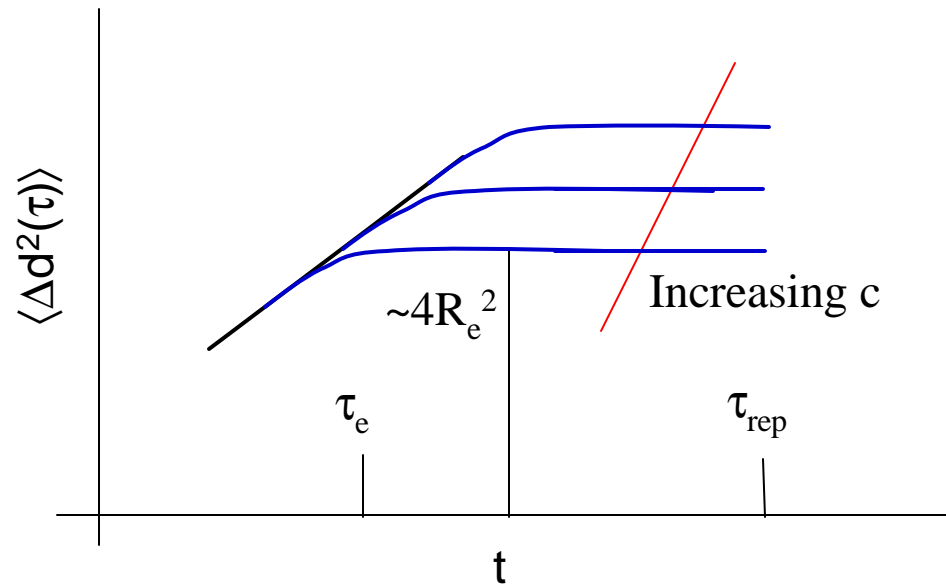
# Transverse displacement from the tube contour

$d(\tau) = \left\{ \begin{array}{l} \text{distance of the middle bead} \\ \text{at } t+\tau \text{ to the closest point of} \\ \text{the chain contour at time } t \end{array} \right\}$

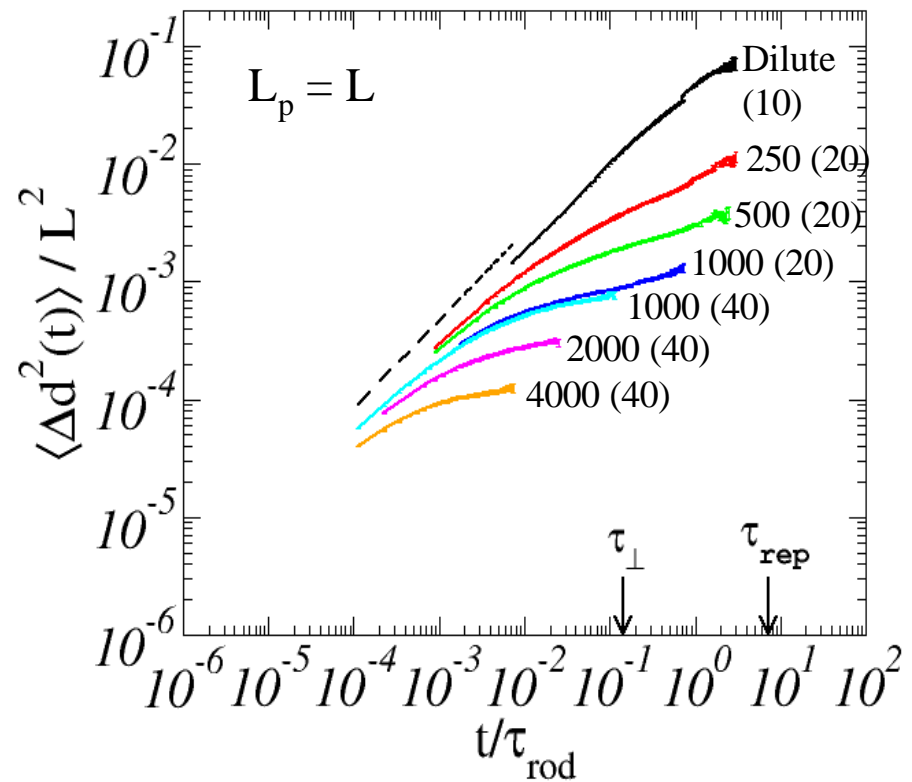
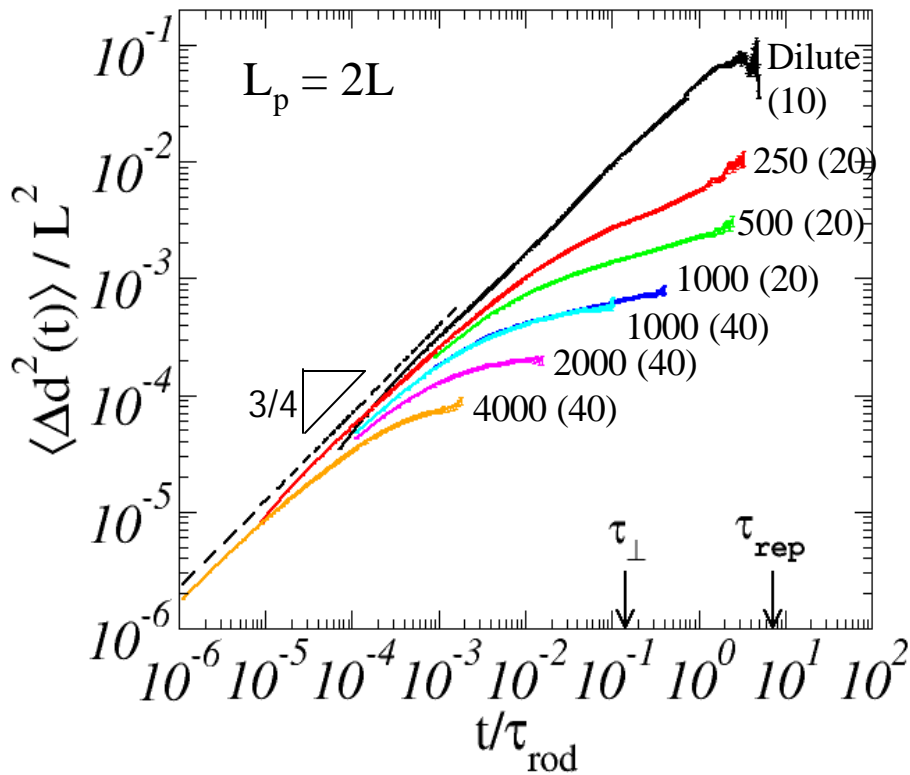


- While calculating  $\langle \Delta d^2(\tau) \rangle = \langle |d(t+\tau) - d(t)|^2 \rangle$ , we include only conformations for which the point of closest approach lies within a segment of previous contour that has never been evacuated.

- Expected behavior



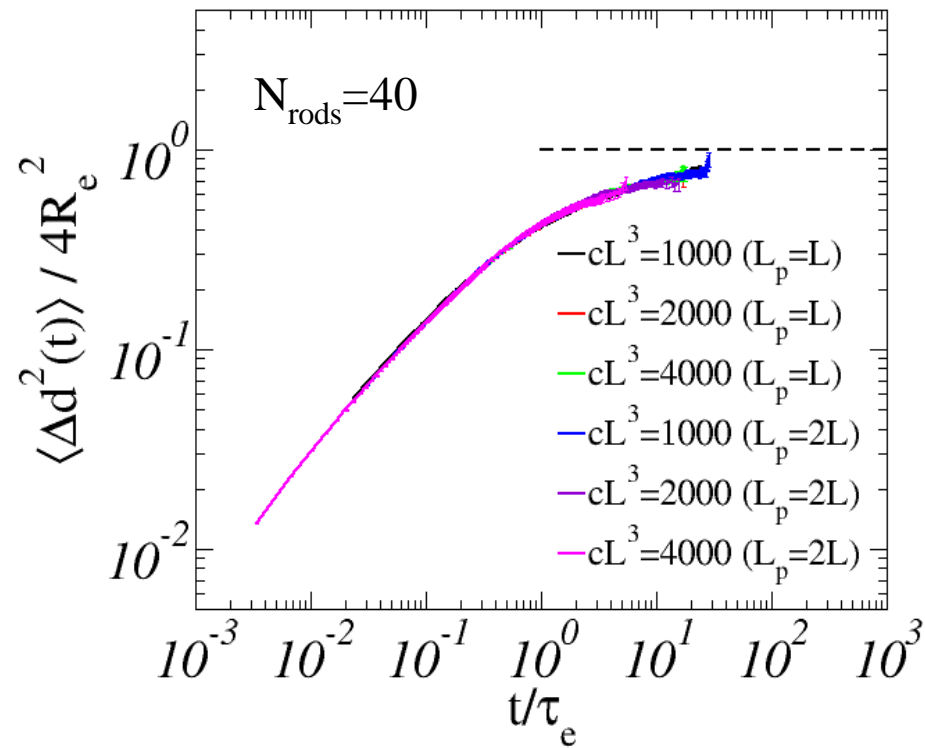
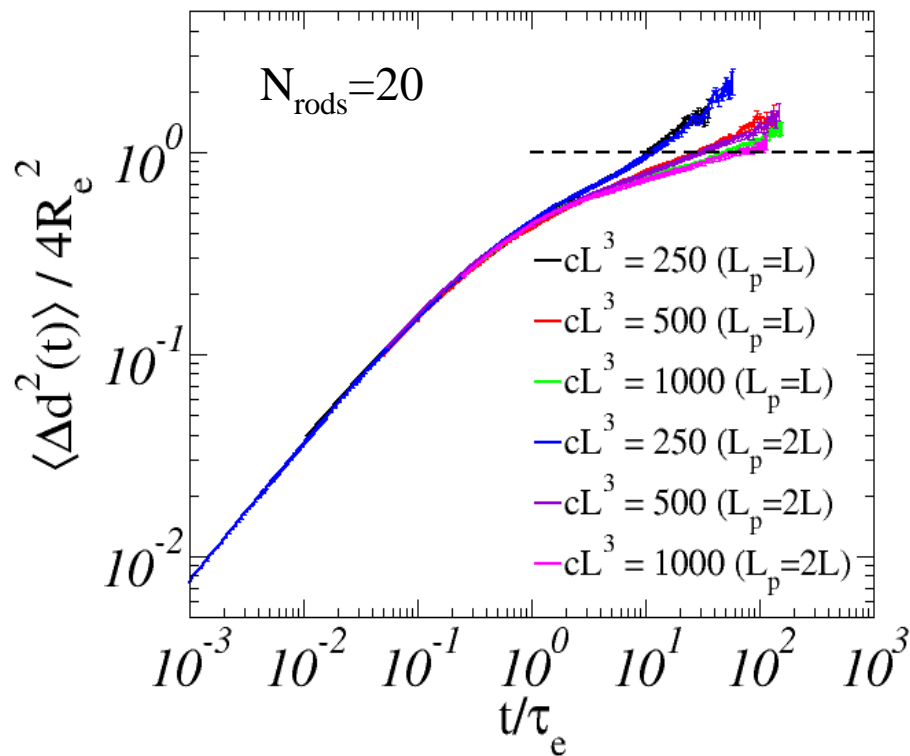
# MSD $\langle \Delta d^2(t) \rangle$ transverse to tube vs time



- Values at ends of lines indicate  $cL^3$  and (in parenthesis) # of rods / chain
- For a wormlike chain,  $\langle \Delta d^2(t) \rangle \propto t^{3/4}$  in dilute solution or for  $t \ll \tau_e$

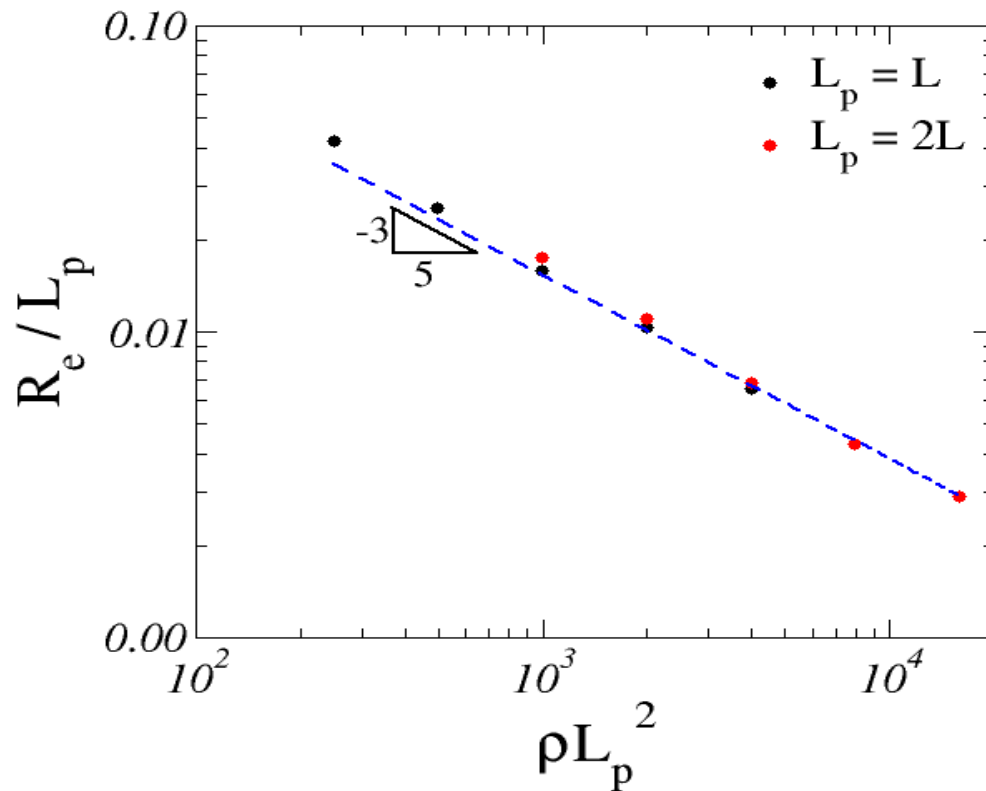
# Scaling collapse of $\langle \Delta d^2(t) \rangle$

- Collapse data by assuming  $\langle \Delta d^2(t) \rangle = 4R_e^2 f\left(\frac{t}{t_e}\right)$
- Because early  $t$  behavior is affected by chain discretization, we collapse data with  $N_{\text{rods}}=20$  and  $N_{\text{rods}}=40$  separately



# Concentration dependence of $R_e$

- $R_e$  and  $\tau_e$  are extracted from shift factors used to collapse data for  $\langle \Delta d^2(t) \rangle$
- By dimensional analysis alone  $R_e/L_p = f(\rho L_p^2, L/L_p)$ , but  $R_e/L_p$  should be independent of  $L/L_p$  in the tightly-entangled regime  $\rho L_p^2 \gg 1$  and  $L \gg L_e$



- For  $\rho L_p^2 = 2000$ , the same tube radius is obtained for chains of different length, and concentration dependence of  $R_e$  agrees with Odijk/Semenov prediction

# Concentration dependence of $\tau_e$

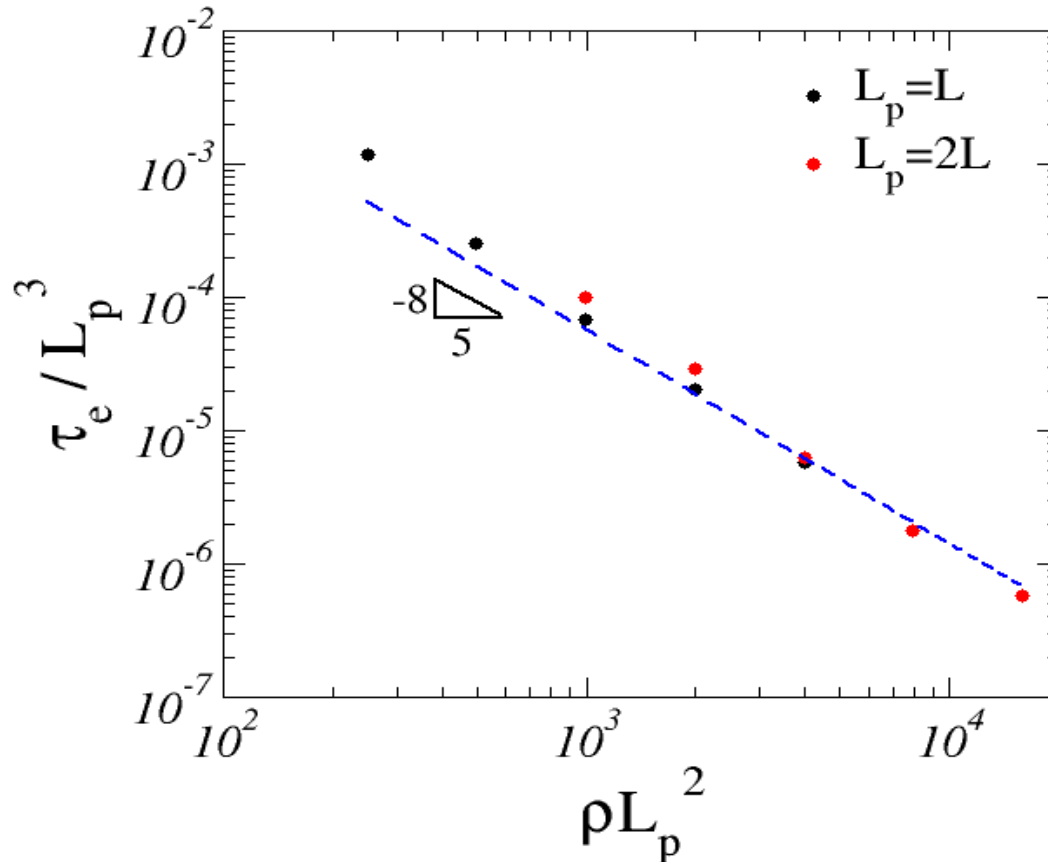
## •Analysis

$$\left\langle \Delta d^2(t) \right\rangle \propto L_p^2 \left( kTt / VL_p^3 \right)^{3/4} \propto t^{3/4} \quad t \ll t_e$$

$$\left\langle \Delta d^2(t) \right\rangle \cong 4R_e^2 \propto L_p^2 \left( rL_p^2 \right)^{-6/5} \quad t \gg t_e$$

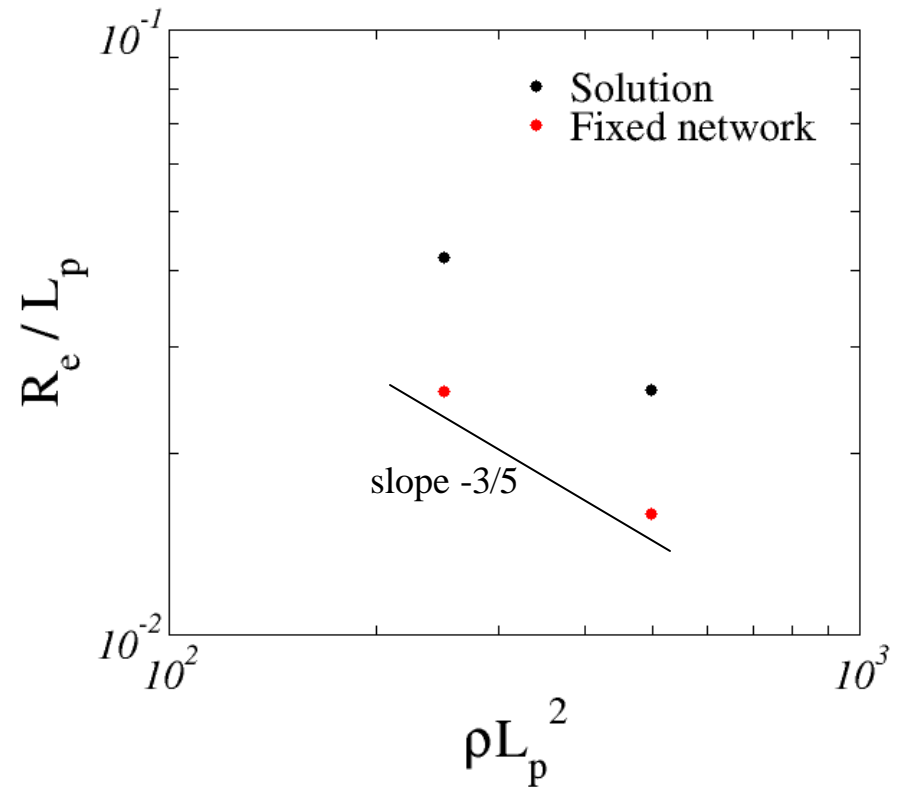
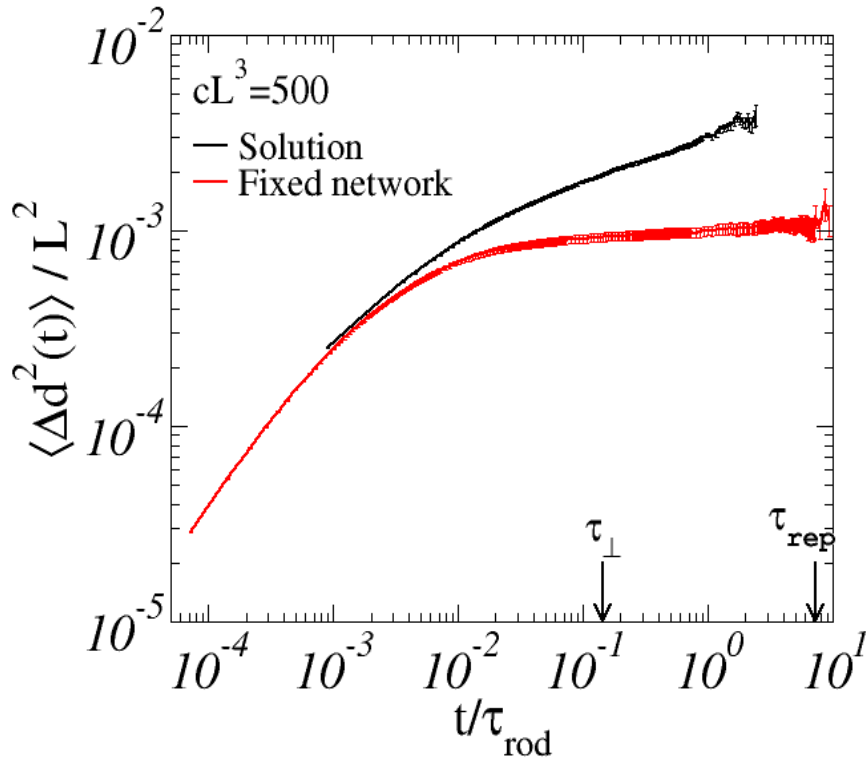
$$\left. \vphantom{\left\langle \Delta d^2(t) \right\rangle} \right\} t_e \cong \frac{VL_p^3}{kT} \left( rL_p^2 \right)^{-8/5}$$

## •Simulation



# MSD Transverse to Tube of Chain in a Frozen Network

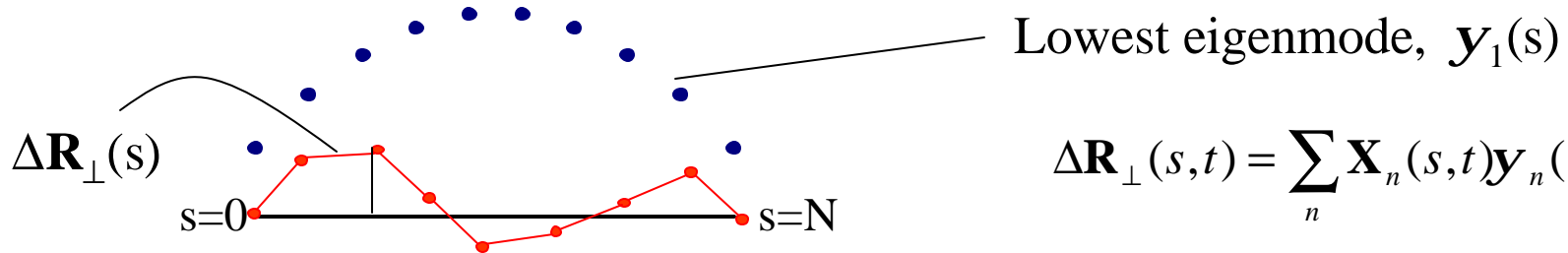
- Construct equilibrated network, then freeze all but one chain.



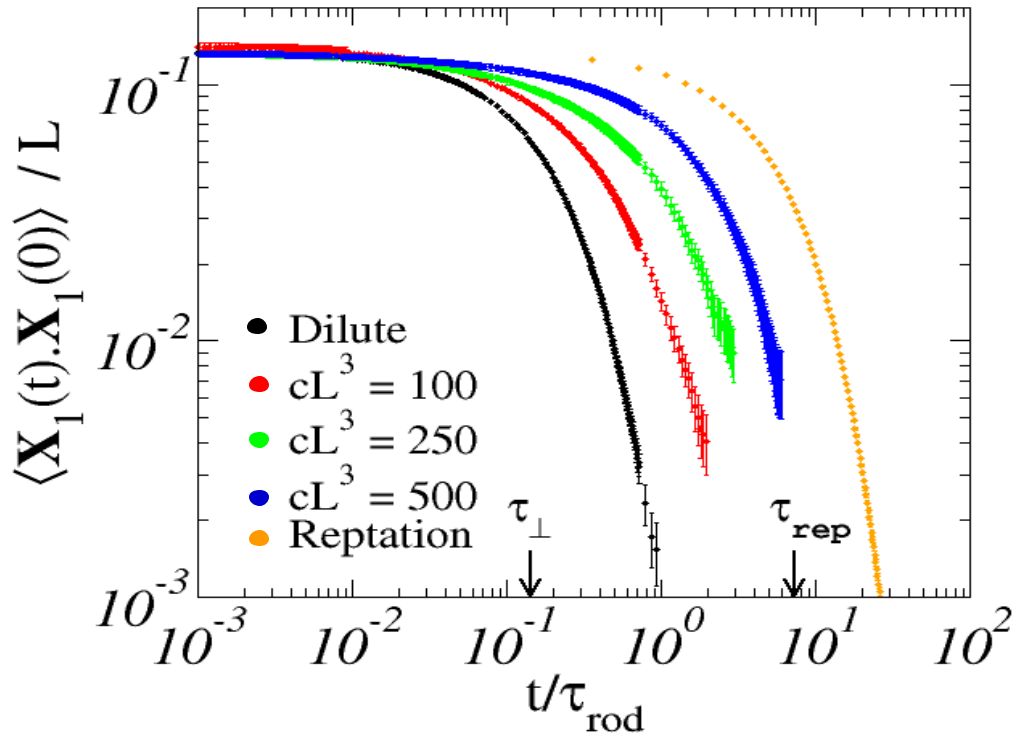
- Significantly narrower tube, with no tendency to widen with time
- Same concentration dependence as in solution:  $R_e \propto \mathbf{r}^{-3/5}$

# Normal Bending Modes

- The transverse dynamics of a chain in dilute solution may be linearized about a straight line, and decomposed into transverse eigenmodes



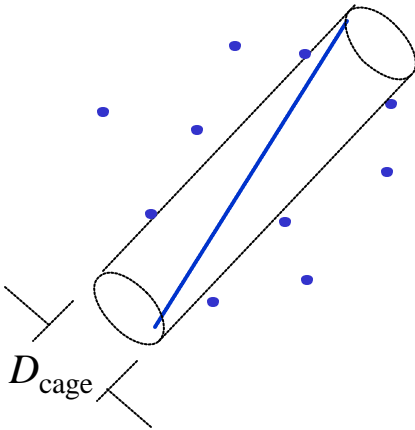
$$\Delta \mathbf{R}_\perp(s, t) = \sum_n \mathbf{X}_n(s, t) \mathbf{y}_n(s)$$



The decay time of the lowest mode increases continuously, and appears to approach  $\tau_{\text{rep}}$

# Rotational Diffusivity - Theory

Doi-Edwards Cage Model  
(Rigid or Loosely Entangled Rods)

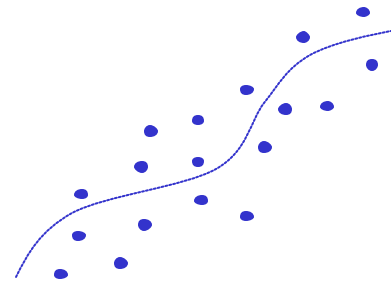


$$D_{\text{cage}} \propto \frac{1}{rL}$$

$$\Delta q \propto \frac{D_{\text{cage}}}{L}$$

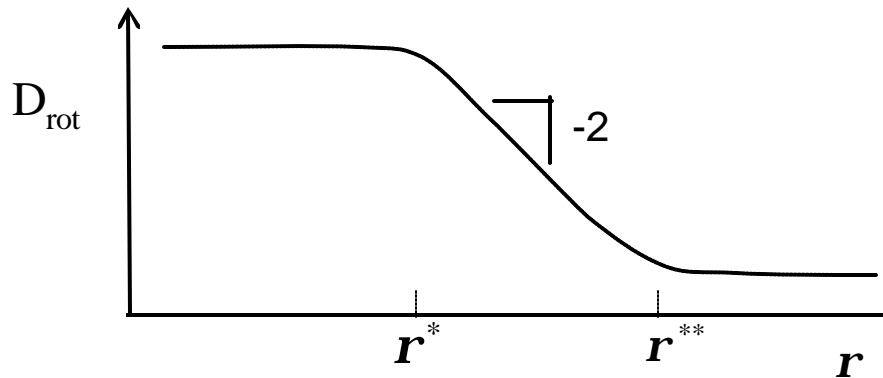
$$D_{\text{rot}} \propto \frac{\Delta q^2}{t_{\text{rep}}} \propto D_{\text{cage}} L^{-4} r^{-2}$$

Reptation along Curved Tube  
(Tightly Entangled Semiflexible Rods)

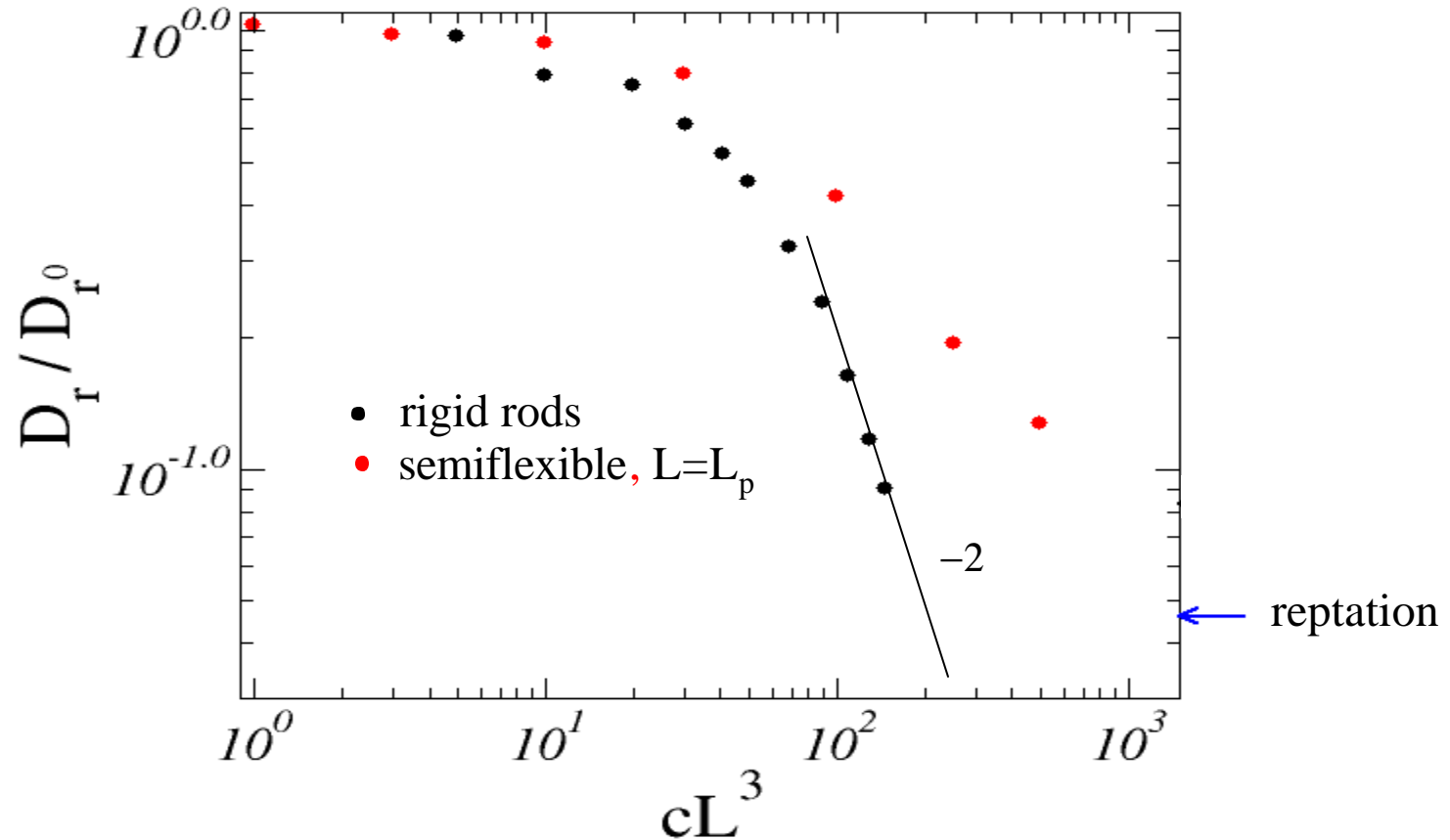


$$\Delta q \propto \frac{L}{L_p}$$

$$D_{\text{rot}} \propto \frac{\Delta q^2}{t_{\text{rep}}} \propto D_{\text{cage}} L_p^{-2}$$



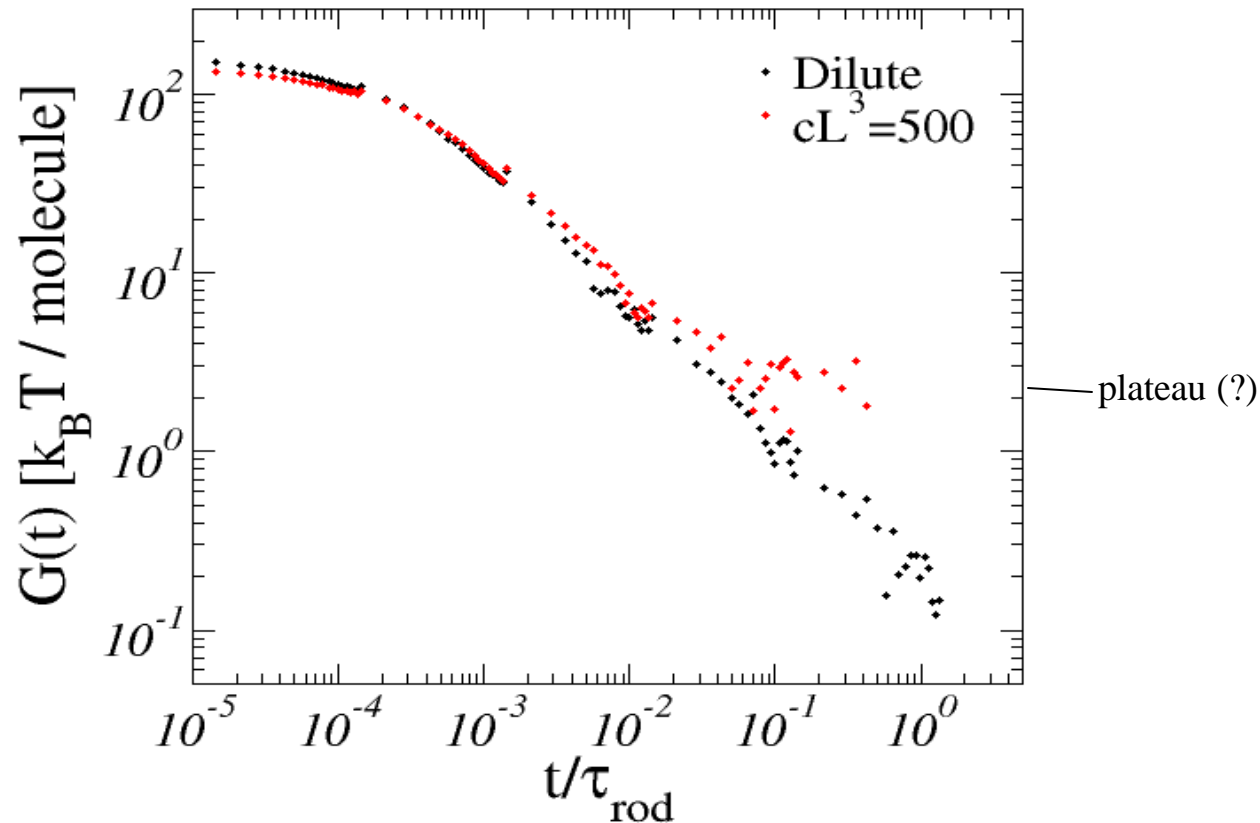
# Rotational diffusivity in concentrated solutions



Rigid rod simulation results from Bitsanis *et. al.*, *Macromolecules*, **21**, 2824; **23**, 1157.

# Linear Viscoelasticity (a preliminary attempt)

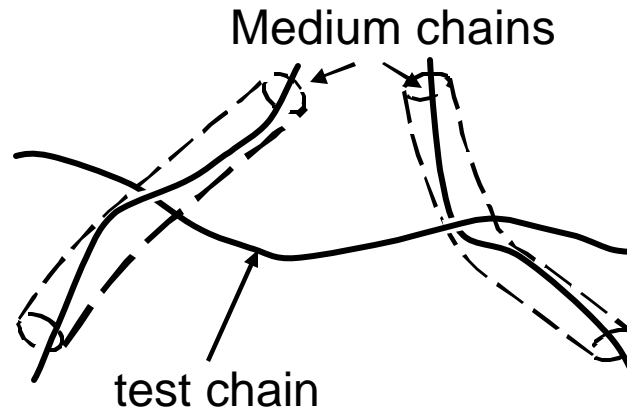
- Relaxation of stress following 10 % uniaxial extension of periodic simulation cell
- Use difference of stress in deformed and undeformed systems with same initial conditions and same sequence of random numbers



- Suggests existence of a plateau with a modulus of about 2  $k_B T$  / molecule

# A Theory of the Tube Diameter

- For short times, or long chains, solution is in a state of constrained equilibrium.
- Confinement free energy  $U_{\text{conf}}[h]$  for a randomly chosen test chain is given by the dependence of free energy of the surrounding network upon the test chain contour



- Approximation: Assume that each medium chain is itself confined to a tube by an approximately harmonic confinement potential.
- Self-consistency: Strength of confinement potential assumed for medium chains must match strength of calculated potential for the test chain.
- Complication: Surrounding medium chains can also undergo *collective* elastic relaxation.

# Binary Collision Approximation

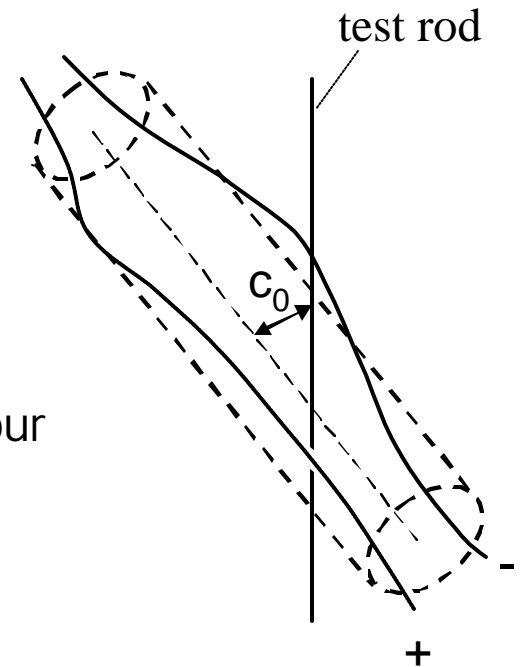
- Thought experiment:
  - a) Insert a rigid test rod suddenly into an entangled solution
  - b) Move it sideways, and measure restoring force
- Focus upon constraint imposed by test rod on fluctuations of one nearby semiflexible medium chain

- Probability that medium chain is trapped in "+" state

$$P_+(c_0) = \int_{c_0}^{\infty} \frac{dh}{\sqrt{2pR_e}} e^{-\frac{1}{2}(h/R_e)^2}$$

$c_0$  = initial distance of rod from "preferred" tube contour  
(i.e., from tube contour in absence of test rod)

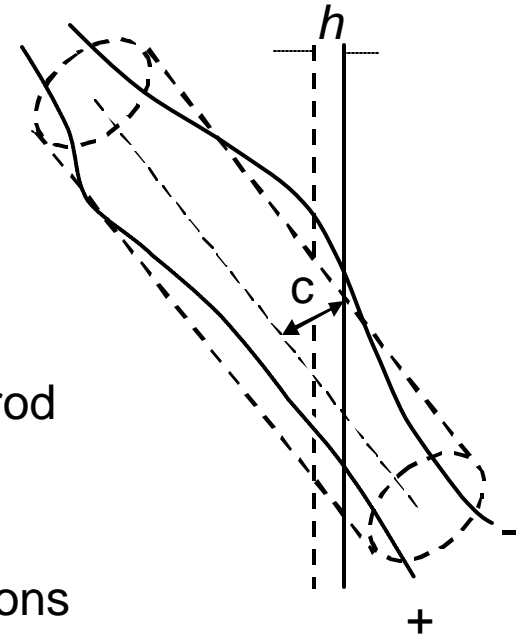
$$R_e^2 \equiv \langle h^2(s) \rangle$$



- Displace test rod sideways a distance  $h$
- Increase in fluctuation free energy of medium chain in the + state due to constraint imposed by test rod

$$A_+(c) = -kT \ln \int_c^{\infty} \frac{dh}{\sqrt{2p} R_e} e^{-\frac{1}{2}(h/R_e)^2}$$

$c$  = distance of tube contour from displaced test rod  
(depends on  $h$  and relative orientation)



- Sum  $A_{\pm}(c)$  over +/- topologies, and over random positions and orientations of medium chain tube contours. This yields average confinement free energy

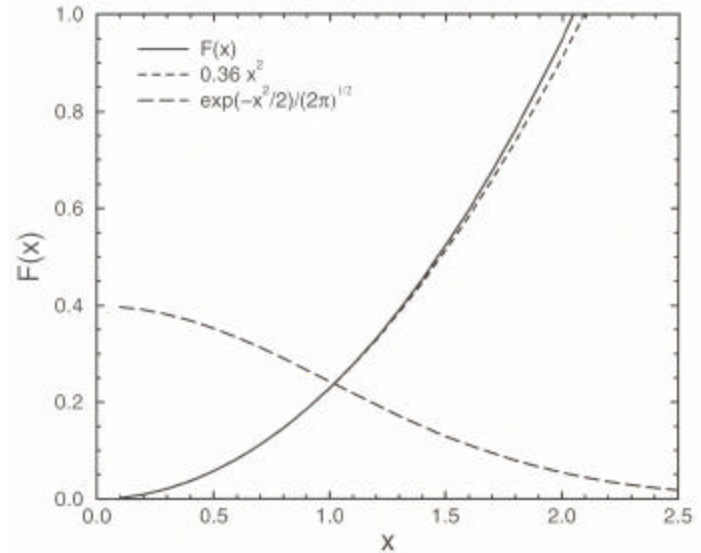
$$\frac{A_{conf}(h)}{L} = r kT R_e F\left(\frac{h}{R_e}\right)$$

- Average potential is nearly harmonic

$$\frac{A_{conf}(h)}{L} = \mathbf{r} kT R_e F\left(\frac{h}{R_e}\right)$$

$$\square \frac{1}{2} \mathbf{g} h^2$$

$$\mathbf{g}(q) \approx 0.72 \mathbf{r} kT / R_e$$



- Refined calculation with a semiflexible test chain yields a spring constant half as large, i.e.,  $\mathbf{g}(q) \approx 0.36 \mathbf{r} kT / R_e$
- Calculate  $R_e^2 \equiv \langle h^2(s) \rangle$  with this potential, and require self-consistency:

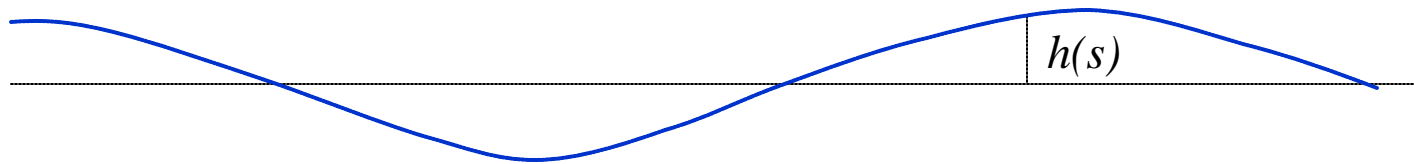
$$R_e^2 \equiv \langle h^2(s) \rangle = \int \frac{dq}{2\mathbf{p} \mathbf{k}} \frac{kT}{q^4 + \mathbf{g}(q; R_e)}$$

- Result is consistent with simple scaling argument, but predicts a prefactor:

$$R_e = 0.80 \mathbf{r}^{-3/5} L_p^{-1/5}$$

# Effective Medium Approximation

- Consider a chain embedded in an elastic continuum with modulus  $G$ . Calculate force  $f(q)$  that resists sinusoidal deformation with wavenumber  $q$



- Problem: If force on medium is exerted along a line, we obtain a logarithmically divergent compliance. If forces on medium are smeared over region of radius  $\mathbf{x}$  around chain, however, continuum mechanics yields

$$\mathbf{g}(q) \equiv \frac{h(q)}{f(q)} \approx \frac{4\mathbf{p} G}{-\ln(q\mathbf{x})}$$

- Proposed cutoff length:  $\mathbf{x} \gg L_e$

Reason: Single chains can transmit forces along their backbones for distances of order  $L_e$

- Require self-consistency with the previous tube model calculation of  $G$

$$G = \frac{7 \mathbf{r} kT}{5} \int \frac{dq}{2\mathbf{p}} \frac{\mathbf{g}(q;G)}{\mathbf{k}q^4 + \mathbf{g}(q;G)}$$

D.M., *Macromolecules*  
Vol. 31, 7044 (1998)

- Self-consistent result for effective medium approximation

$$R_e \gg \mathbf{r}^{-1/2}$$

$$G \gg kT \mathbf{r}^{4/3} L_p^{-1/3}$$

vs. binary collision approximation

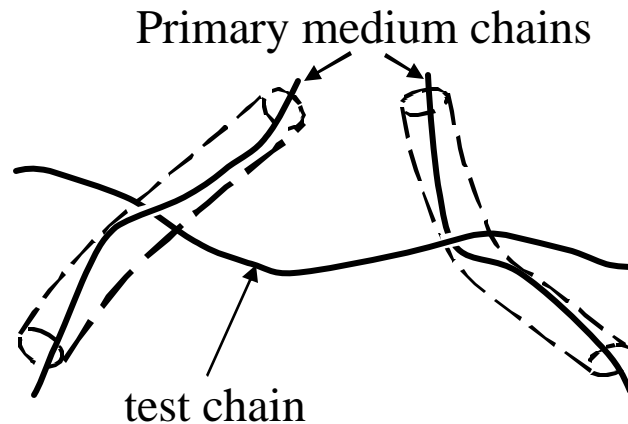
$$R_e \gg \mathbf{r}^{-3/5} L_p^{-1/5}$$

$$G \gg kT \mathbf{r}^{7/5} L_p^{-1/5}$$

- Effective medium theory predicts a wider tube in the limit  $\mathbf{r} L_p^2 \gg 1$ , and thus presumably yields the correct limiting behavior.

# Elastic Network Approximation (ENA)

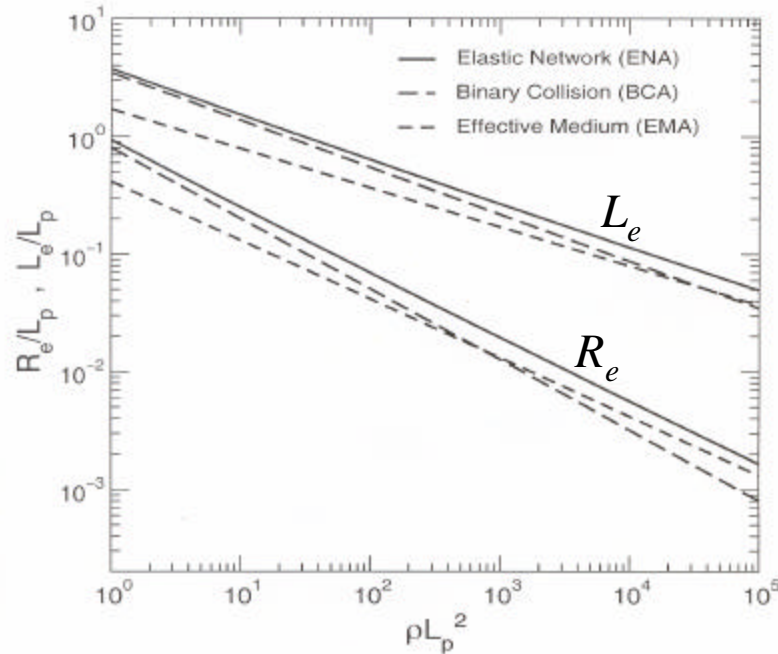
- Transmission of force from test chain to network is treated as a two step process
  - i) The test chain exerts forces directly upon a few “primary” medium chains
  - ii) Tube contours of primary medium chains are embedded in a continuum



- Force exerted on “continuum” = - Confining force on primary medium chains  
(This effectively smears force distribution over a region of radius  $L_e$ )
- Test chain displacement is sum of displacement of elastic medium (EMA) and displacement relative to medium (BCA). Add compliances:

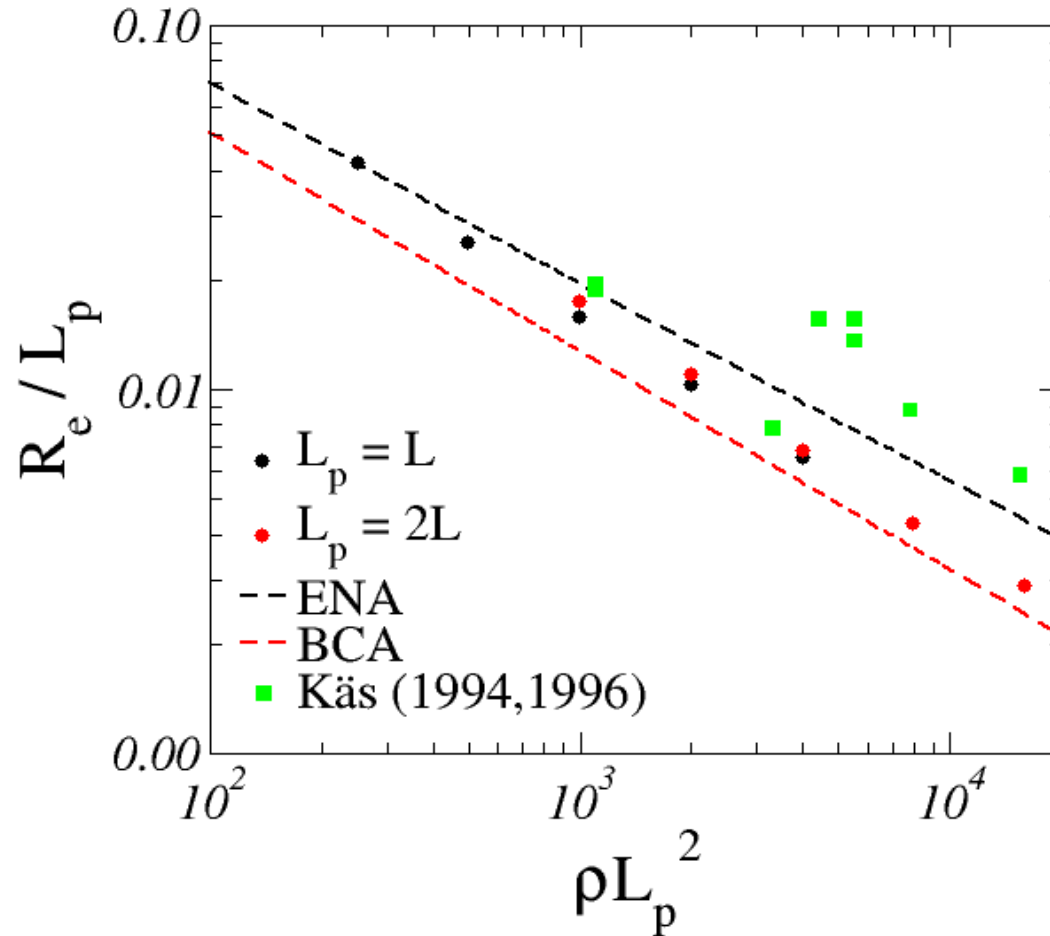
$$\frac{1}{\mathbf{g}(q)} \square \frac{1}{\mathbf{g}_{BCA}(q)} + \frac{1}{\mathbf{g}_{EMA}(q)}$$

# Predictions for Tube Radius and Entanglement Length



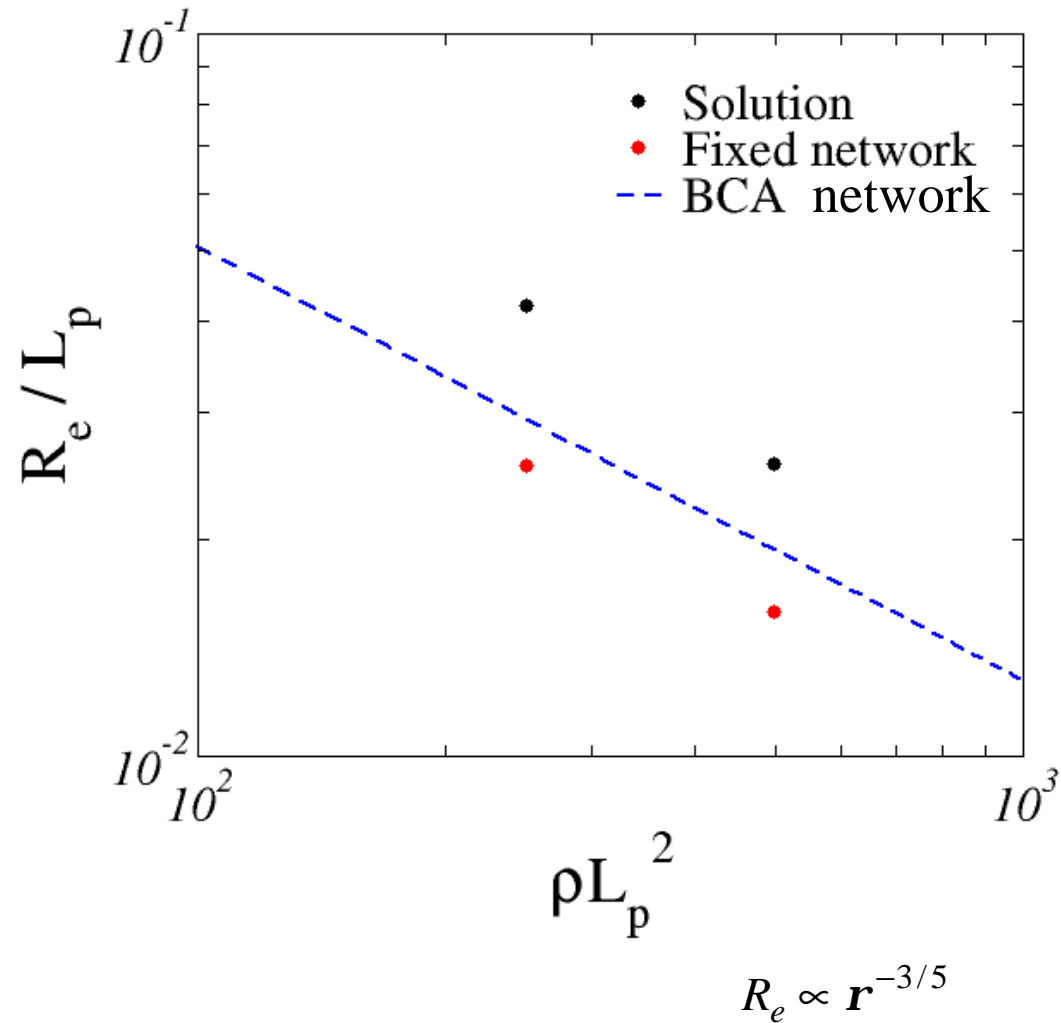
- For F-actin with  $c = 0.1 - 1.0$  mg/ml,  $\rho L_p^2 = 10^3 - 10^4$
- ENA predicts a broad crossover from binary collision to effective medium predictions for  $R_e$  near  $\rho L_p^2 = 10^3$

# Tube Radii from Theory, Simulations, and Experiment



- No evidence for the predicted crossover to  $\rho^{-1/2}$  concentration dependence
- ENA predicts slightly wider tube than found in simulations
- Experimental data are scattered, but seem to yield wider tube than simulations

# Theory and Simulation for a Chain in a Frozen Network



# Conclusions

- Simulations of semiflexible rods with  $L=L_p$  show onset of tight entanglement (significant suppression of transverse bending fluctuations) for  $cL^3 > 100$
- Tube radius exhibits a concentration dependence  $R_e \propto r^{-3/5} L_p^{-1/5}$  above a crossover concentration

$$c^{**} L^3 \cong 10^3 \sqrt{L_p / L}$$

- These results suggest that solutions of PBLG and FD virus near their IN transitions, for which  $cL^3 < 500$ , are within a crossover to tight entanglement, while solutions of long F-actin filaments, for which  $cL^3 = 500 - 5,000$ , can become tightly entangled .
- Statistical mechanical theory of the tube diameter is in "reasonable" agreement with simulations of solutions (within a factor of 2), but simulations yield no evidence for behavior predicted by effective medium theory.
- Quantitative understanding of tightly-entangled limit provides a limit for behavior of entangled flexible polymers with increase stiffness or concentration.
- Ongoing work
  - Viscoelasticity - stress decay after small amplitude step strain
  - Excluded volume effects