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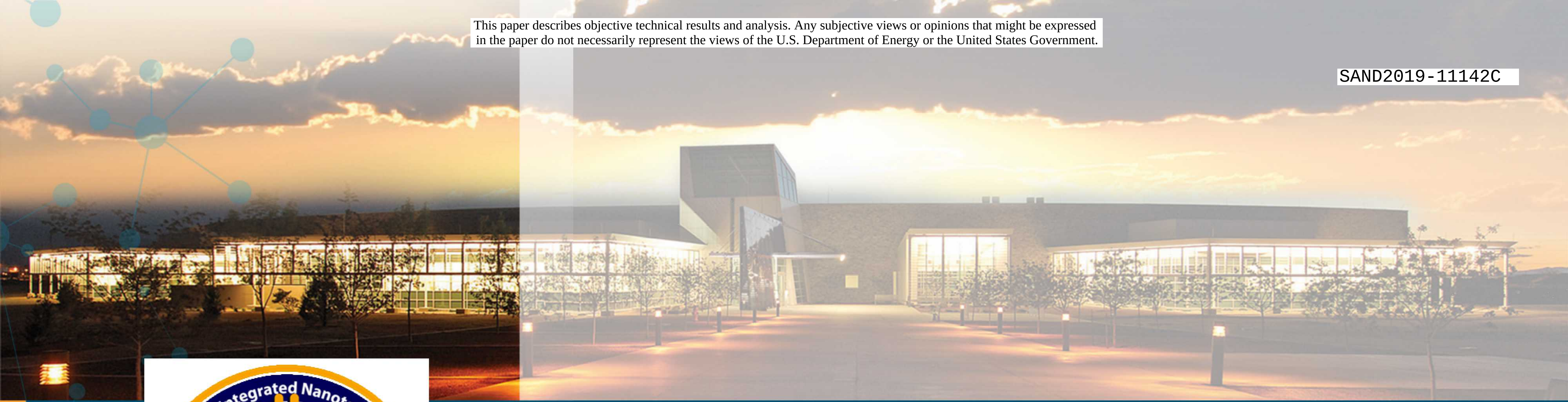

Recent Results in Polyelectrolyte Simulations

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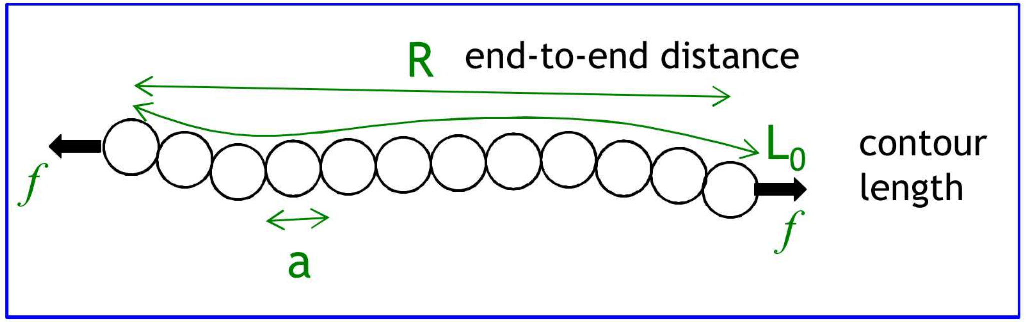
Simple Model for Polyelectrolytes

"All ion" simulations: MD

bead (spring) flexible polyelectrolyte

<u>F = bond + entropy + electrostatics</u>



every bead in polymer is charged

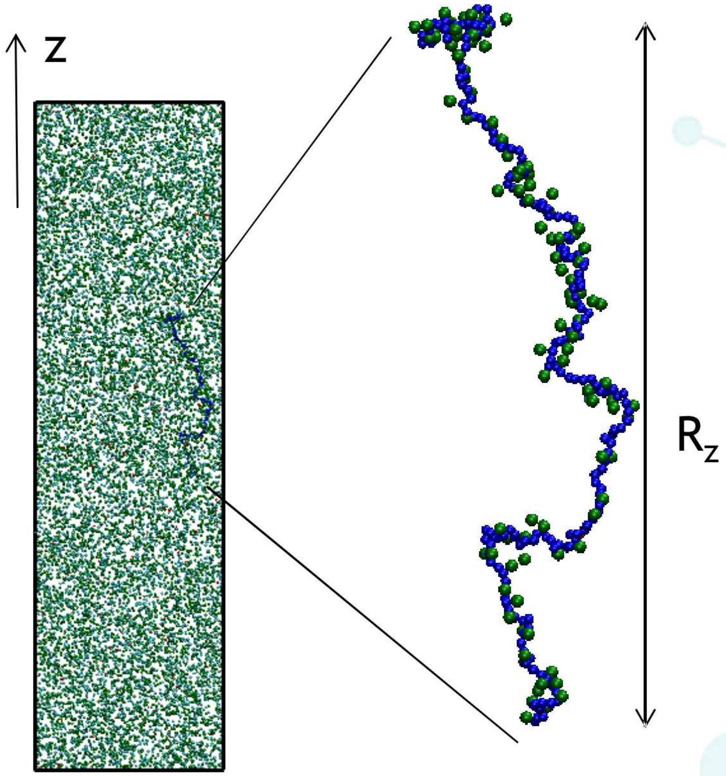
a = 6.4 Å = 0.96 σ (ssDNA spacing)

l_B = 1.065 σ (Bjerrum length) [dielectric continuum]

N = 200

L_0 = (N-1) a = 192 σ

Force-extension simulations



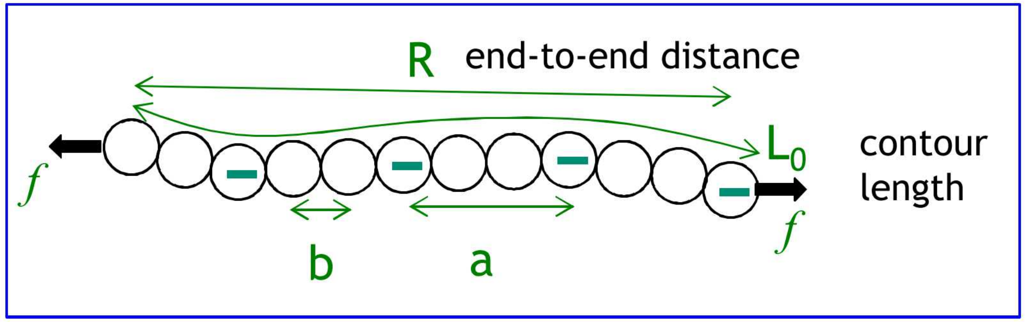
20 mM monovalent

f = 0.20 ε/σ

Additional Features

$b = 0.96\ \sigma$ bond length

$a = m\ b$ charge spacing is varied



Intrinsic stiffness:
add angle term to potential

$U_{angle} = k_a\ (1+\cos\theta)$ $\theta_0 = 180^{\circ}$

Comparison of Experimental and Simulation Data (ssDNA)

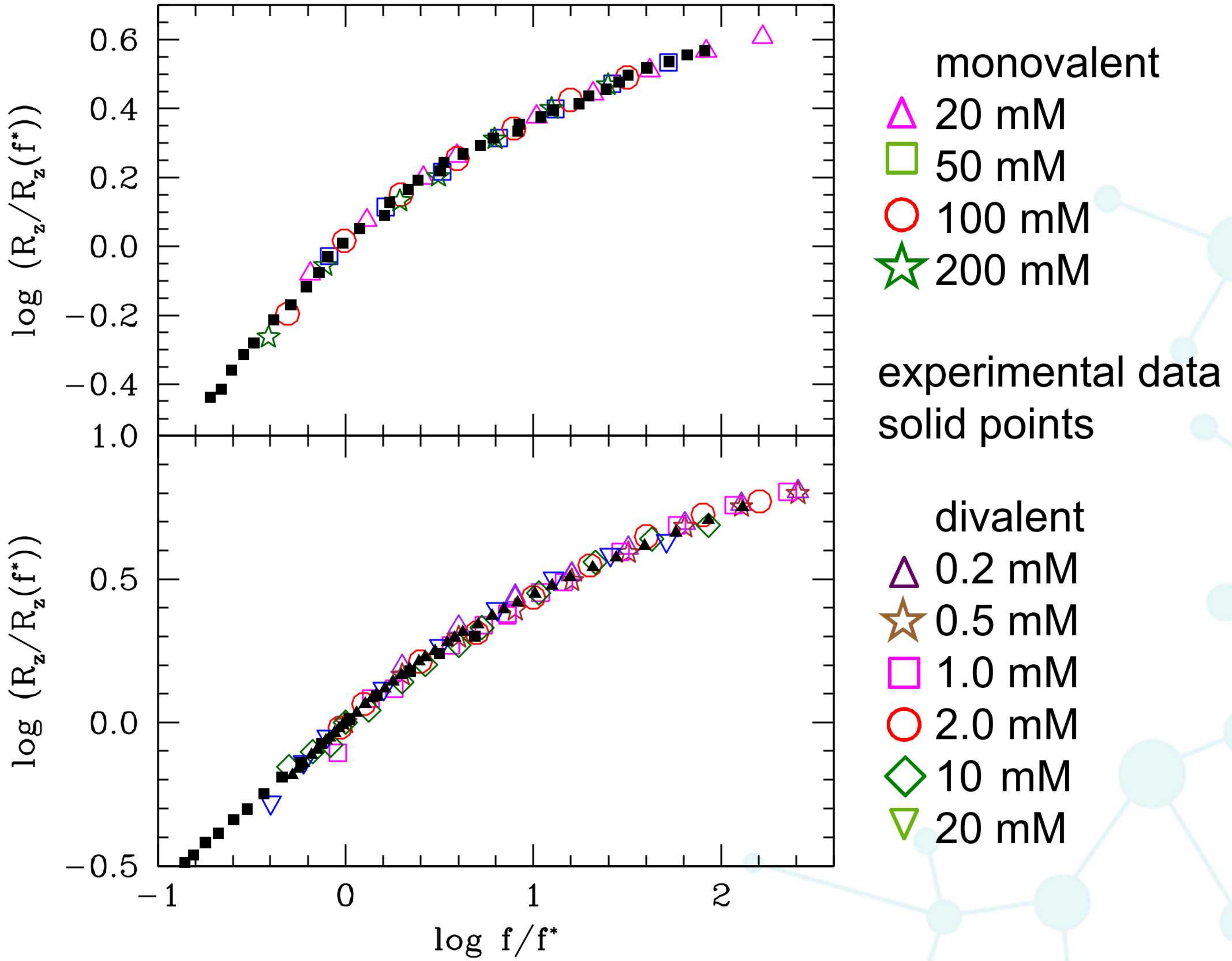
Same scaling procedure as experiments

Simple model is sufficient.

electrostatics, entropy, connectivity

Dustin McIntosh, Omar Saleh, UCSB

Force Extension Curves



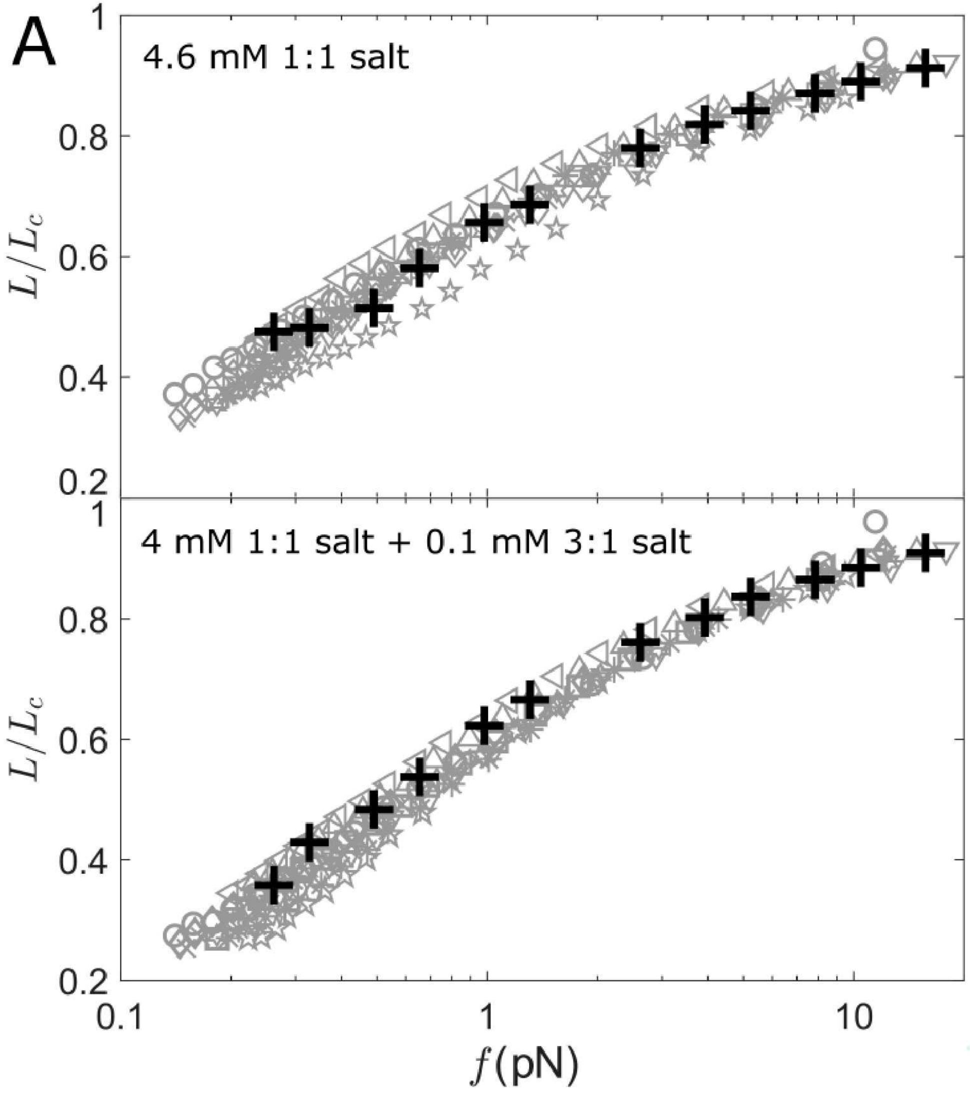
Hyaluronic Acid

Persistence length of 5 nm

Overlap of simulation and experimental data

Simple model works for a variety of polyelectrolytes

Force-Extension



✚ simulation data

Pincus Tension Screening

Tension blobs (Pincus, Macromolecules 1976)

$\xi = k_B T / f$ is tensile screening length

where the excluded volume renormalization is the substitution of the Flory radius[4] $R_F \simeq N^\nu a$ for the ideal chain radius $R_0 = N^{1/2}a$. However, as the chain stretches, its average monomer density decreases leading to a weakening of the excluded volume effect. Thus for sufficiently large external forces, we expect to eventually recover ideal behavior with $\bar{Z} \propto N$ rather than $\bar{Z} \propto N^{2\nu}$ as given by (I.2). This crossover will be described in terms of a competition between a "tensile screening length" $\xi_t = (\beta f)^{-1}$ and the Flory radius R_F. For weak stretching $R_F/\xi \ll 1$, the de Gennes result (eq I.2) should be correct; for stronger stretching with $R_F/\xi_t \gg 1$, we expect to find a modified elastic behavior with $\bar{Z} \propto N$. To find the stress–strain relationship in this limit, we are tempted to employ a scaling argument. Let us assume that the average end-to-end separation may be written as

that its Laplace transform

$$\Gamma_\rho(\mathbf{r}) = \sum_{N=0}^{\infty} \Gamma_N(\mathbf{r}) e^{-N\rho} \qquad \text{(II.1)}$$

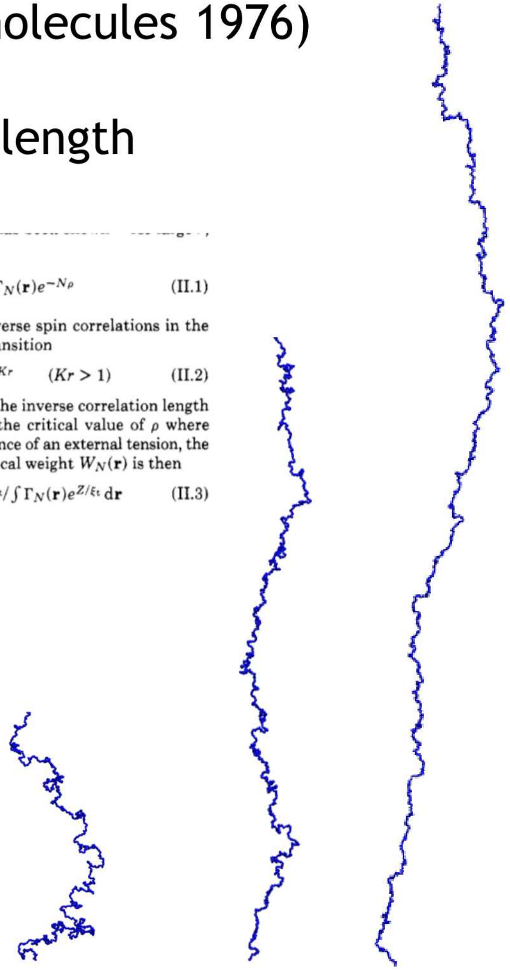
behaves similarly to the transverse spin correlations in the vicinity of a magnetic phase transition

$$\Gamma_\rho(\mathbf{r}) \simeq A(a/r)e^{-Kr} \qquad (Kr > 1) \qquad \text{(II.2)}$$

where A is a function of ρ and the inverse correlation length $K = a^{-1}(\rho - \rho_c)^\nu$ where ρ_c is the critical value of ρ where $\int \Gamma_\rho(\mathbf{r})\, d\mathbf{r}$ diverges. In the presence of an external tension, the appropriate normalized statistical weight $W_N(\mathbf{r})$ is then

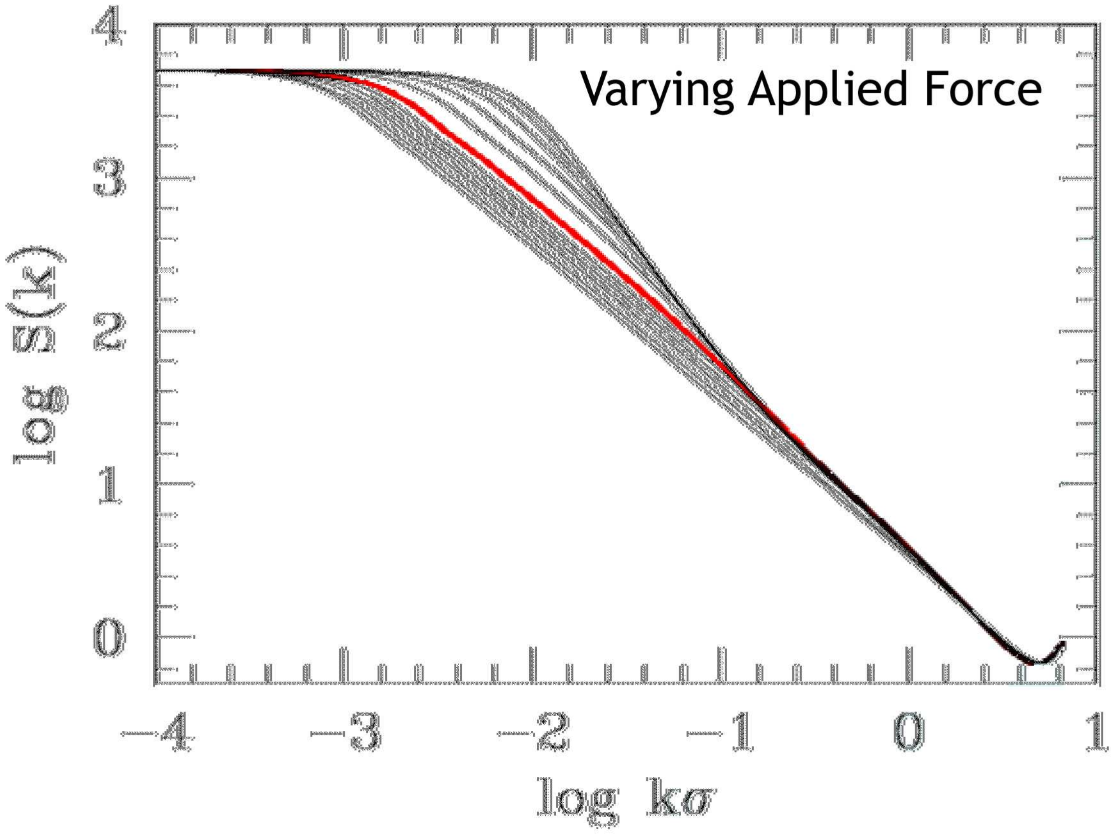
$$W_N(\mathbf{r}) = \Gamma_N(\mathbf{r}) e^{Z/\xi_t} / \int \Gamma_N(\mathbf{r}) e^{Z/\xi_t}\, d\mathbf{r} \qquad \text{(II.3)}$$

leading to

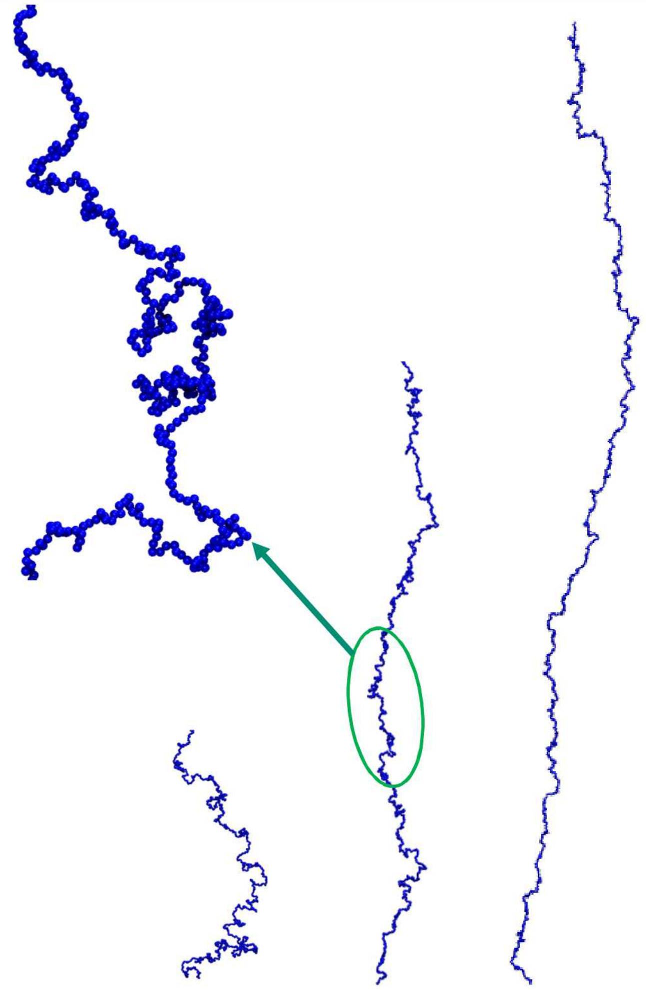


fl_B/kT=0.027 0.112 0.27

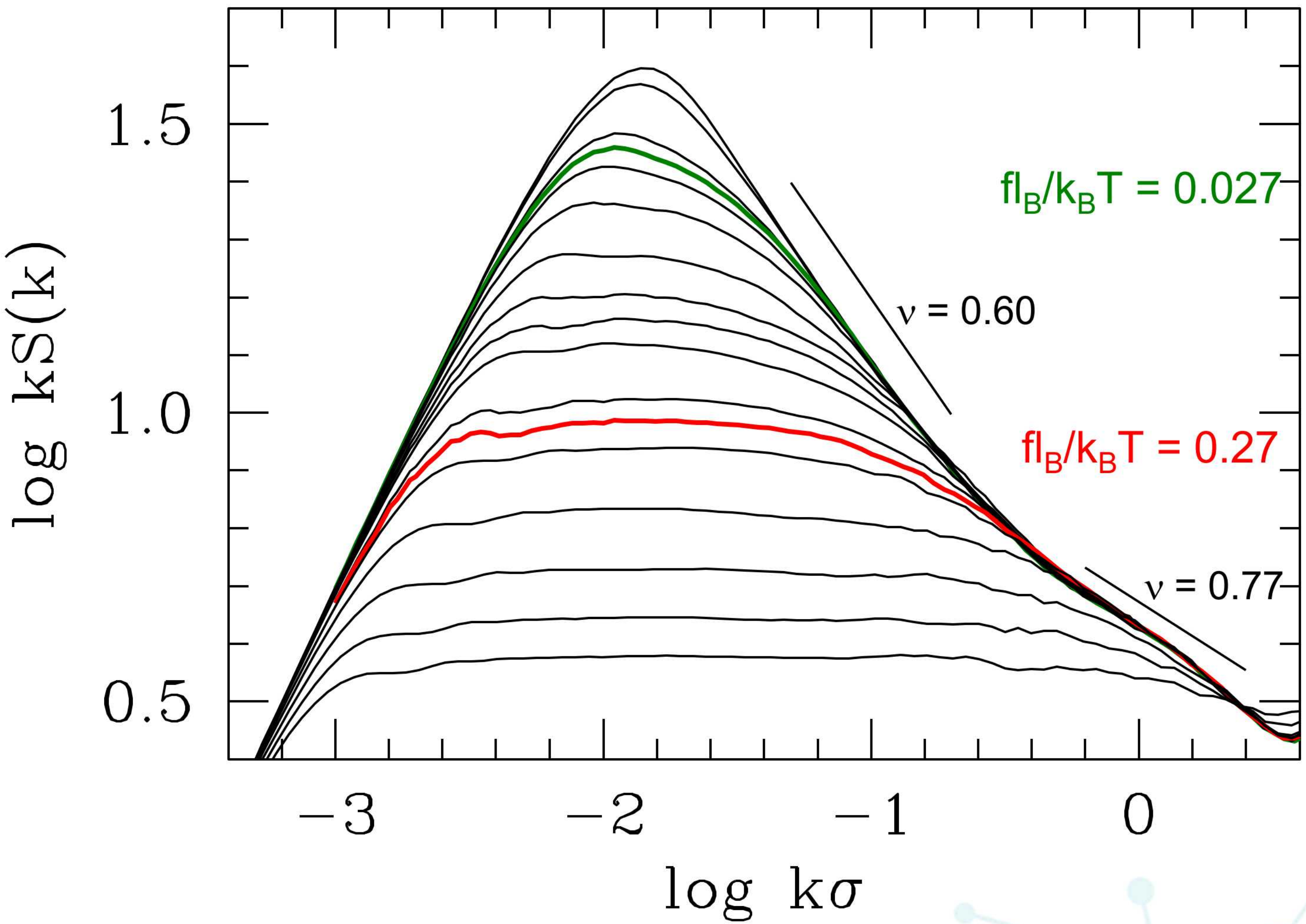
N=5000 ssDNA
200 mM



Structure Factor for N=5000 at 200 mM



fl_B/kT=0.027 0.112 0.27



<u>Region</u>

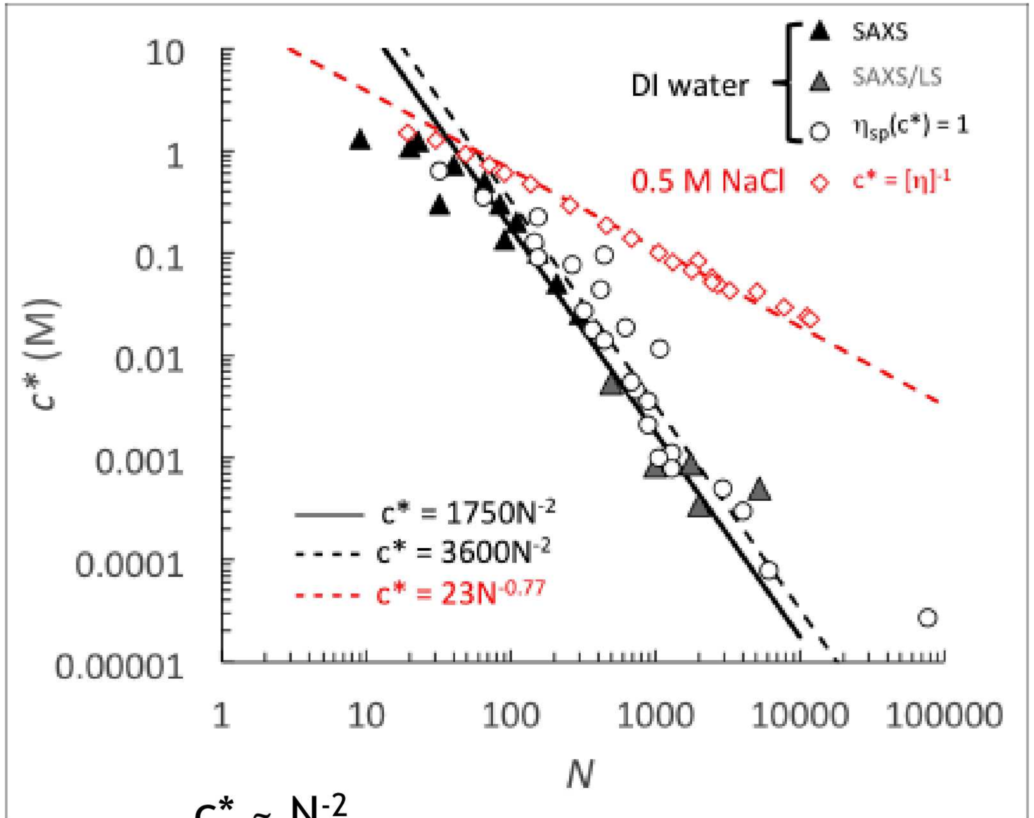
Rotational

Pincus

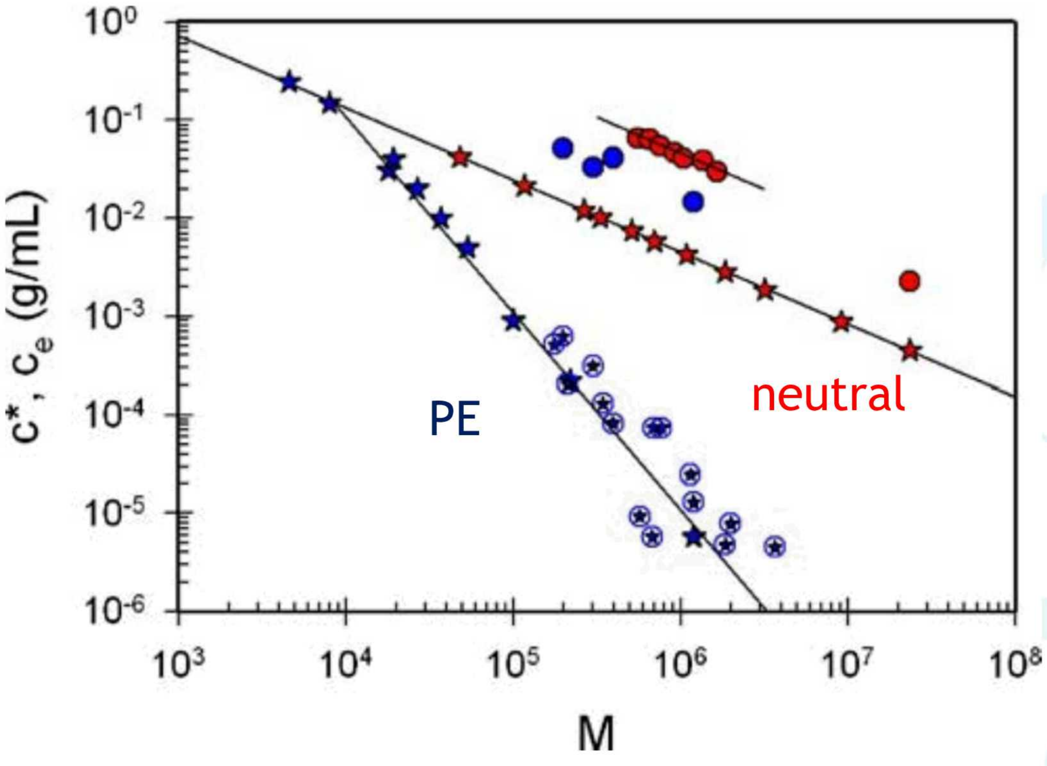
logarithmic

Polyelectrolytes in Solution: Overlap concentration

Lopez 2019



Colby Rheol Acta 2010



$c^* \sim N^{-2}$

if $R \sim N^1$ and $c^* = MN/V \simeq MN/(M\pi R^{*3}/6)$, then $c^* \sim N/N^3 = N^{-2}$

Simulations of Polyelectrolyte Solutions

"All ion" MD simulations

M = 27,..., 800 number of chains

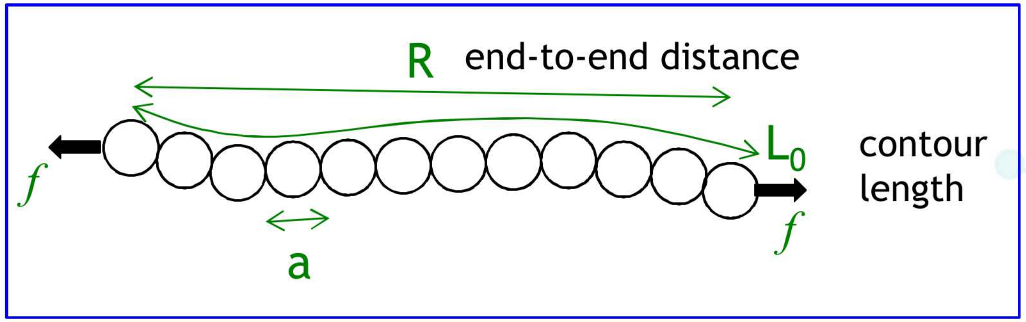
salt free

Bjerrum length = charge separation

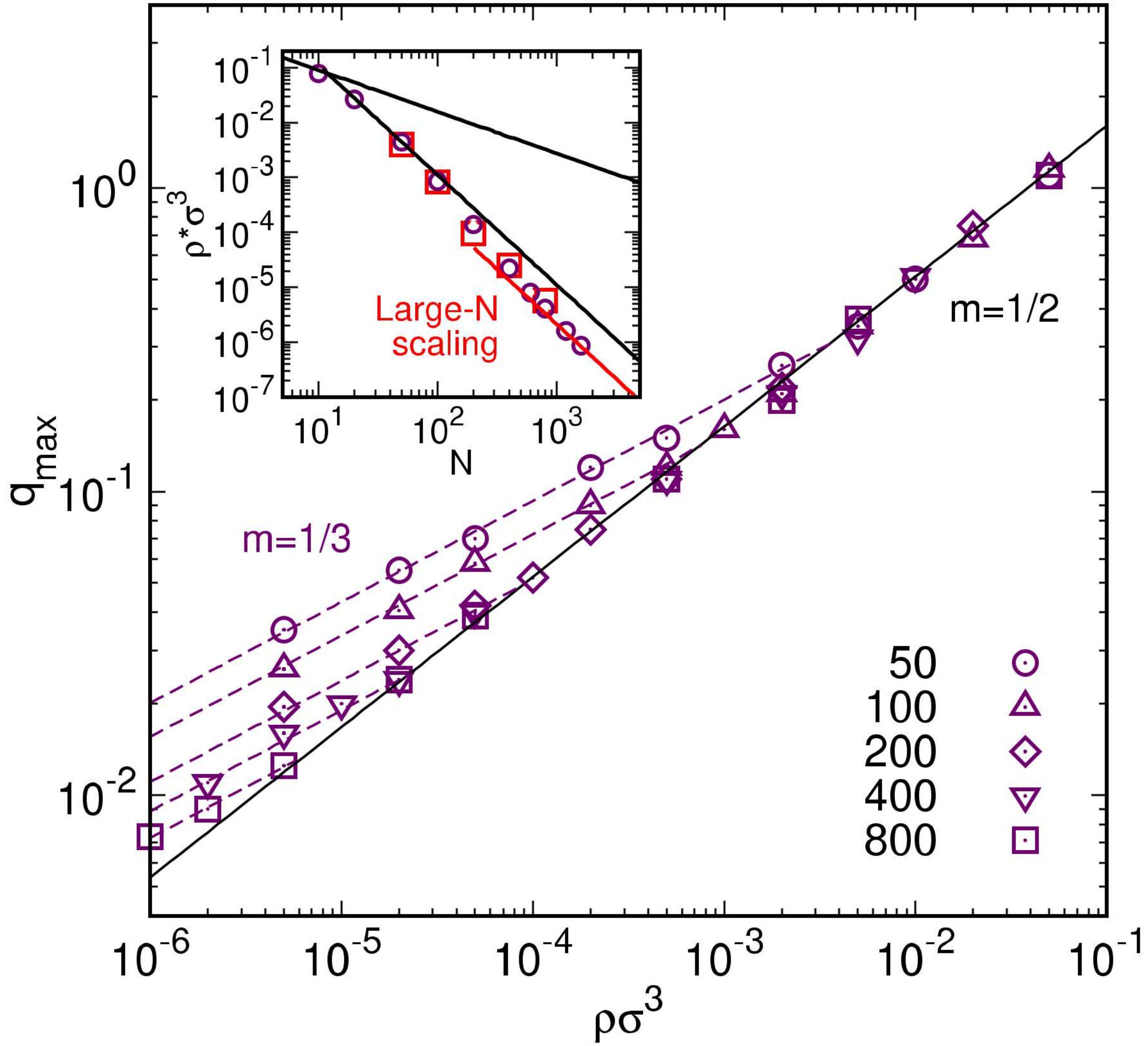
strong polyelectrolyte

F = bond + entropy + electrostatics

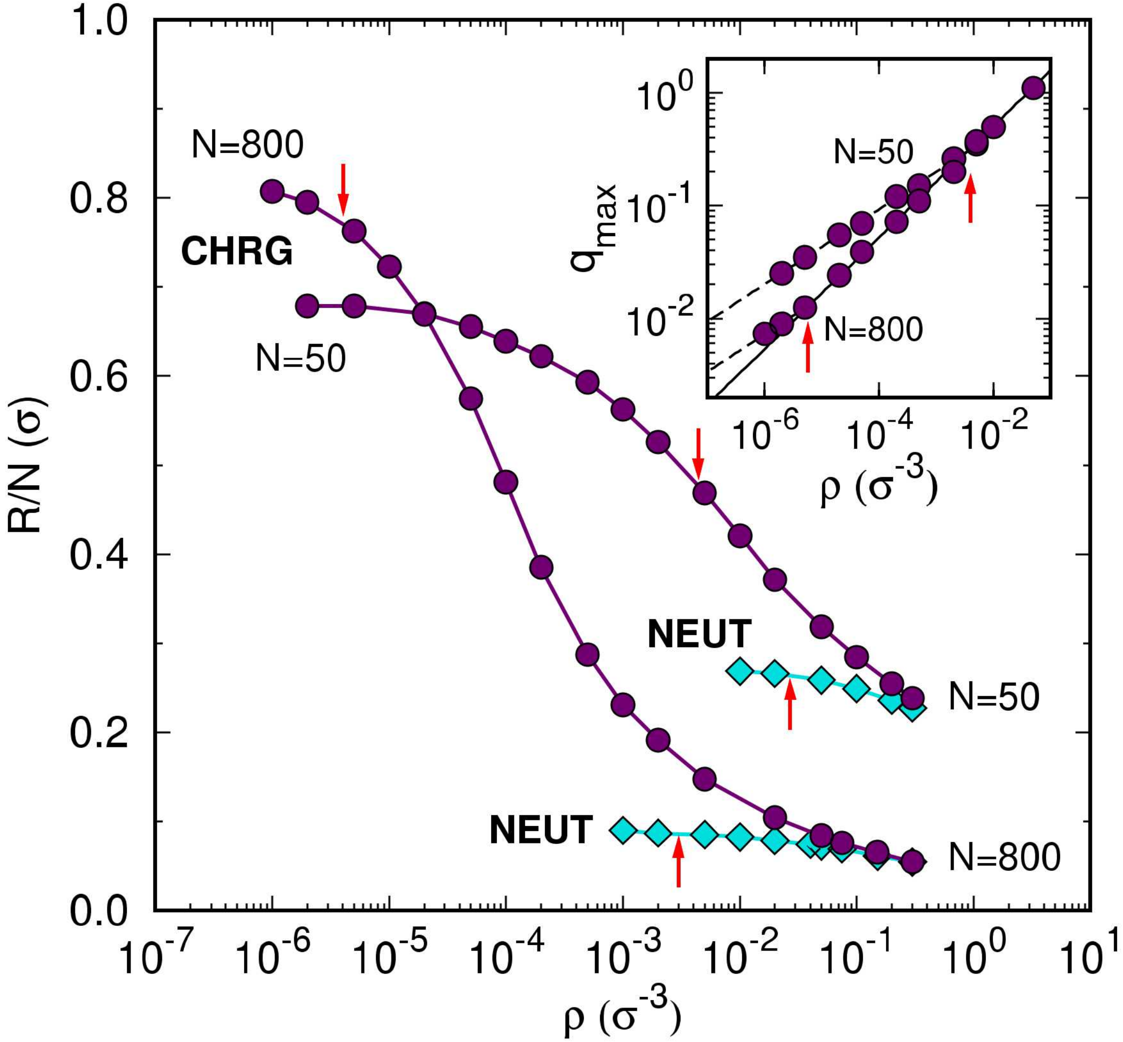
very large N: up to 1600



Overlap from Scattering Data in Simulations



End-to-End Distance



Overlap Methods

Scattering:

transition between $q^{1/2}$ and $q^{1/3}$

Packing:

contact between spheres of diameter R

packing fraction = random close packed

$0.64 = \phi = M \pi R^3/6V = \rho \pi R^3/6N$

Comparison:

N=50

chain expands below ρ*

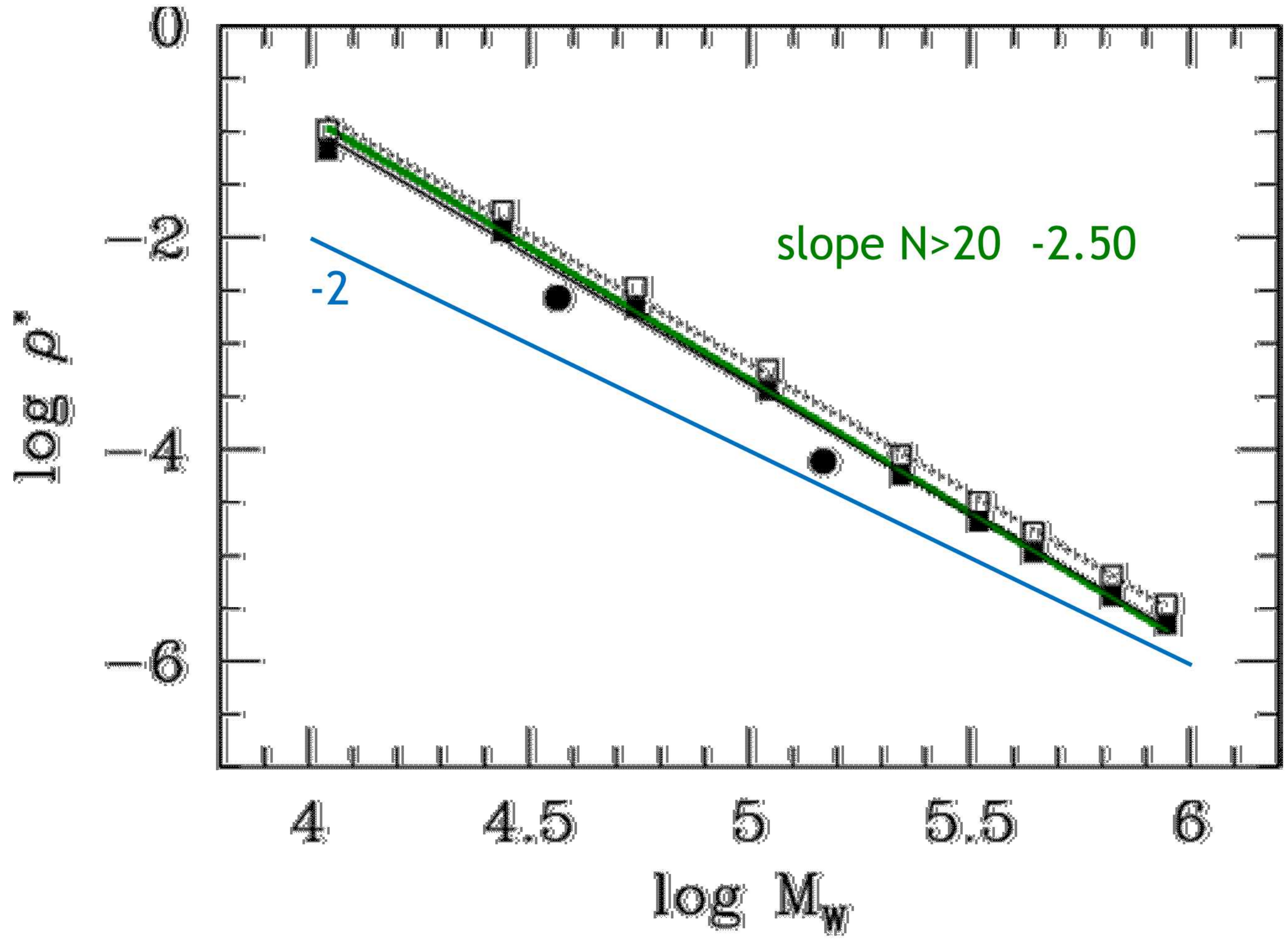
chain bends in 3 linear segments at ρ*

N= 800

chain barely expands below ρ*

chain is 1 linear segment at ρ*

Overlap concentration: Simulation



squares

N=20, ..., 1600

Map 1: 3 NaPSS monomers to 1 bead

volume of monomer

Map 2: units map of volume

Circles:

1 NaPSS monomer to 1 bead

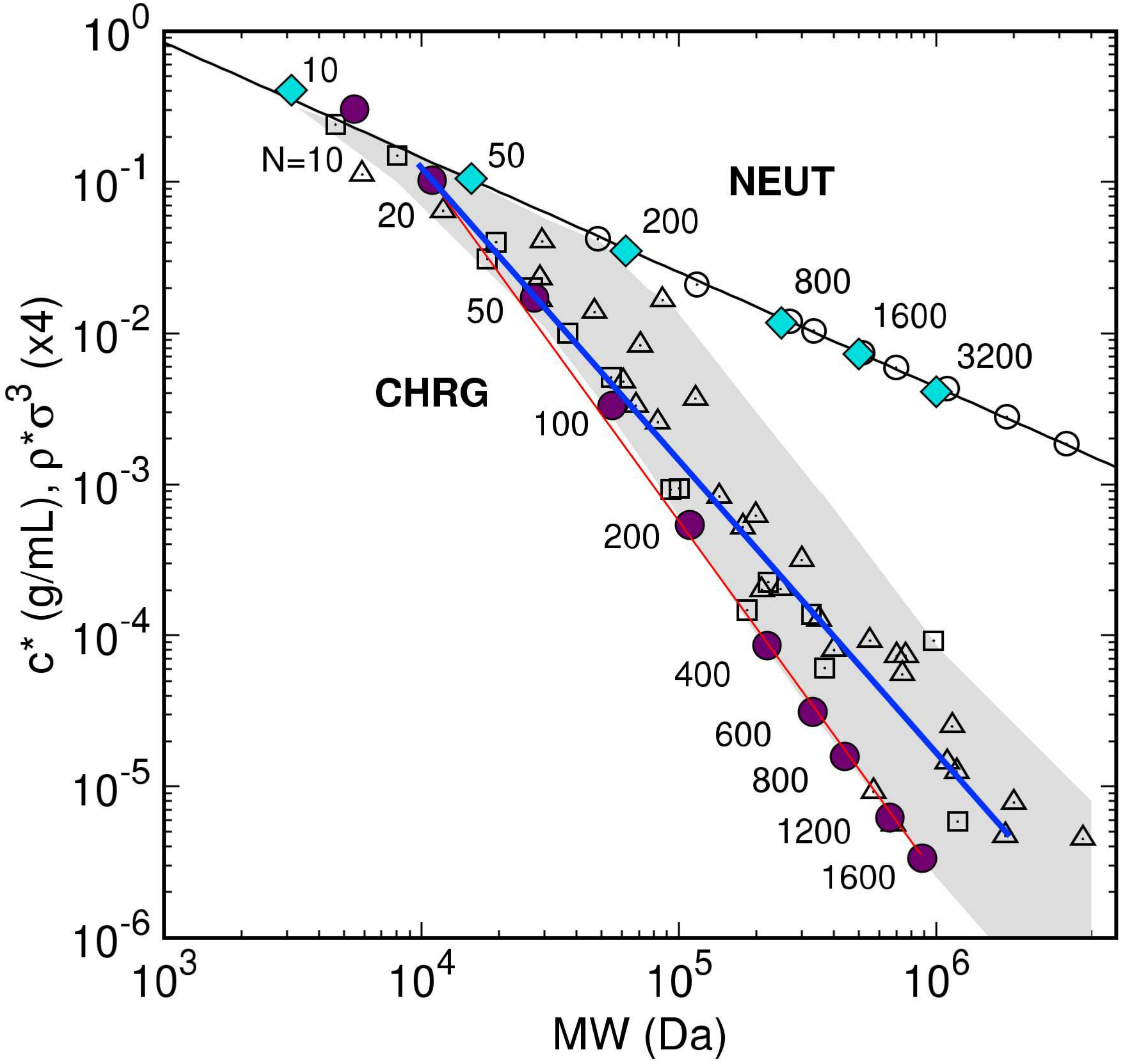
N=200, 800

charge separation in NaPSS = 2.82Å

0.96 σ = 2.82Å σ=2.94Å

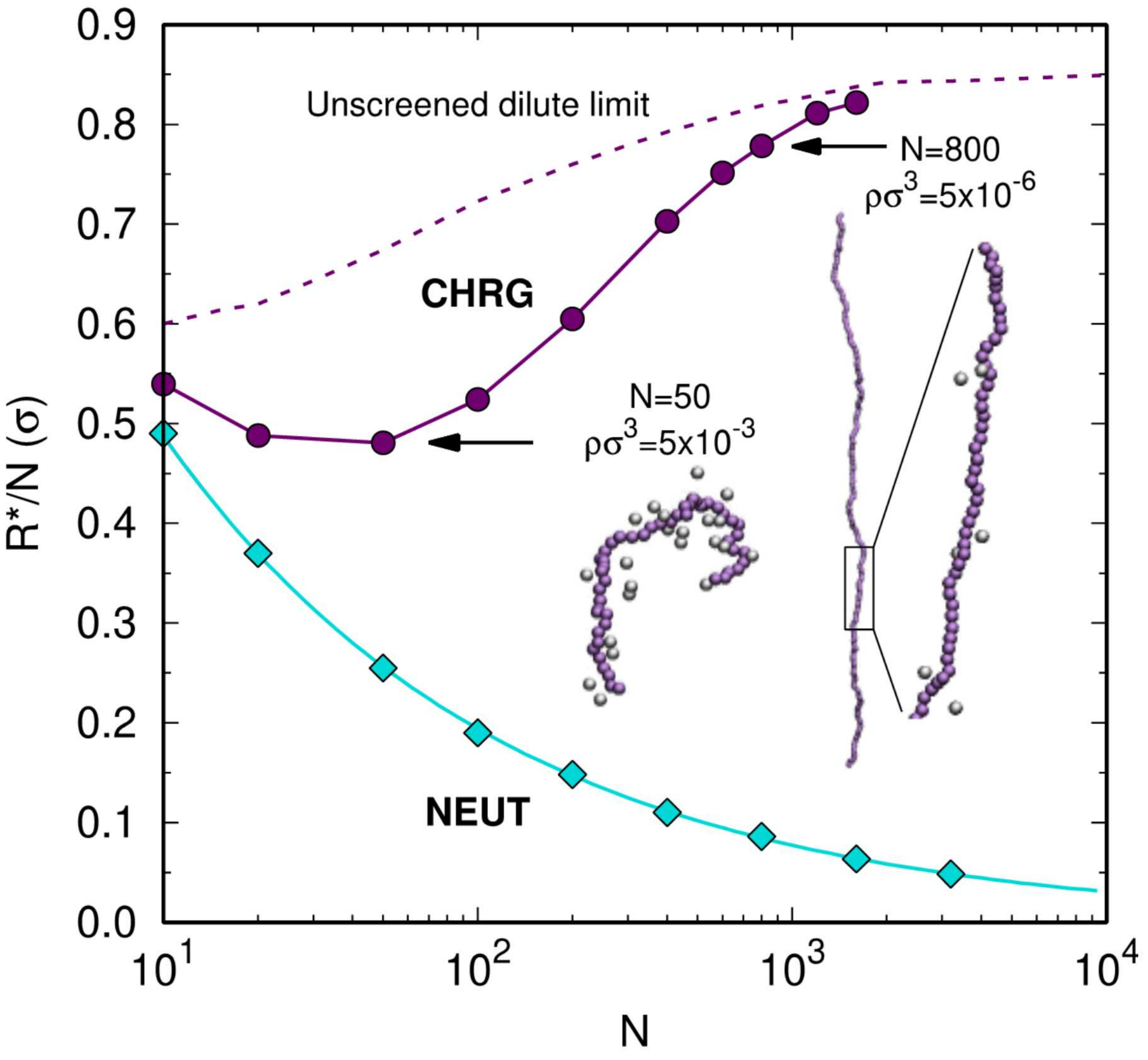
l_B = 7.1Å = 2.41 σ

Overlap Concentration



Map 1: 3 NaPSS monomers to 1 bead

End-to-End Distance at Overlap vs. N



N=50 not fully stretched at ρ^*

N=800 fully stretched at ρ^*

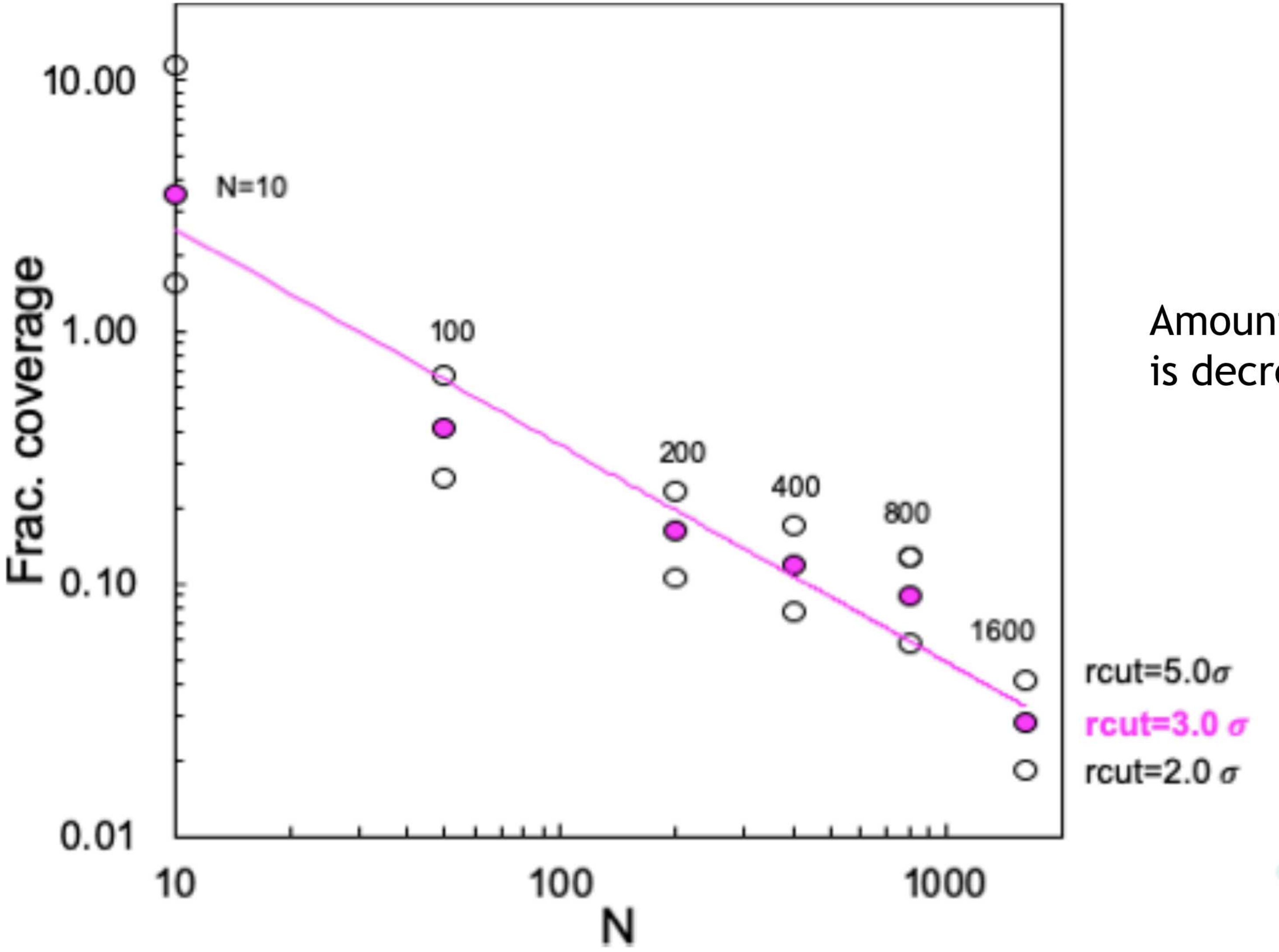
R/N not constant => $R \nsim N^1$

By $N \simeq 800$ getting close to upper limit

Large N limit does not occur until large N

Counterions

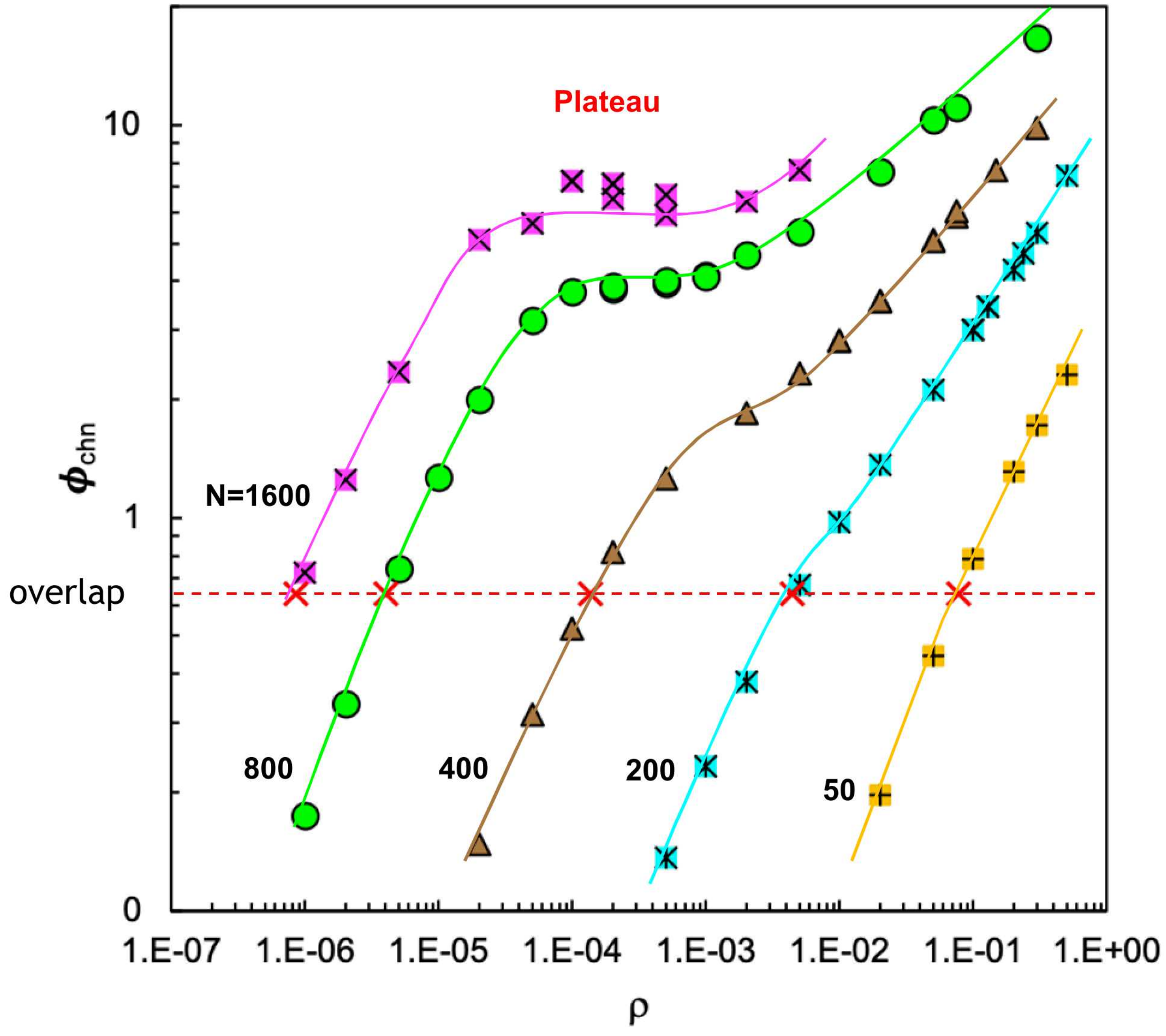
N_{cc}/N



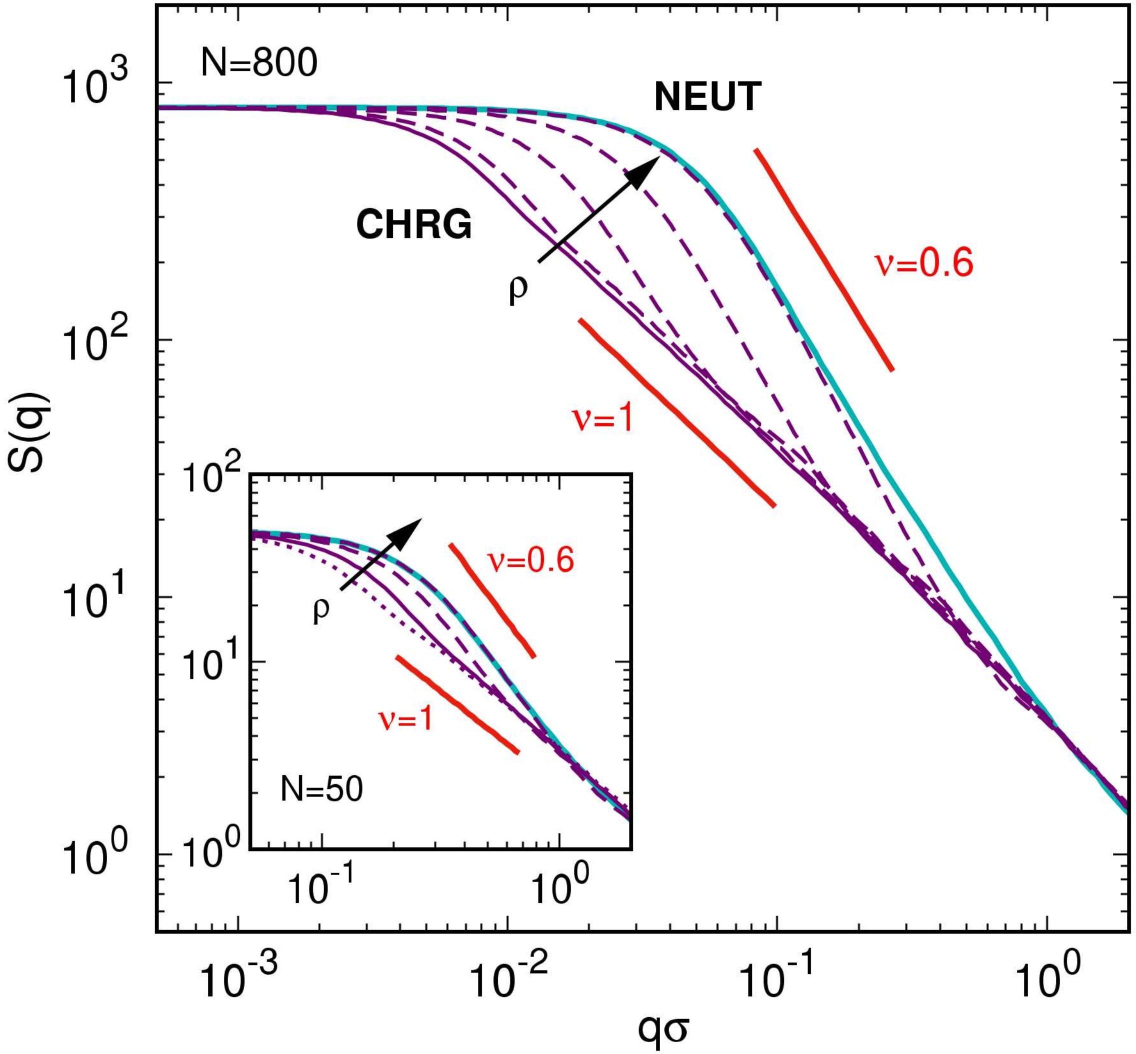
Amount of condensed counterions is decreasing with N and ρ^*

Packing of chains

$\phi = M \pi R^3/6V$



Structure as a function of density



Two changes in S(q) as a function of decreasing ρ:

1) long *q* dependence changes from neutral behavior toward $\nu \simeq 1$
2) transition point decreases =>
   'rodlike' segment get larger

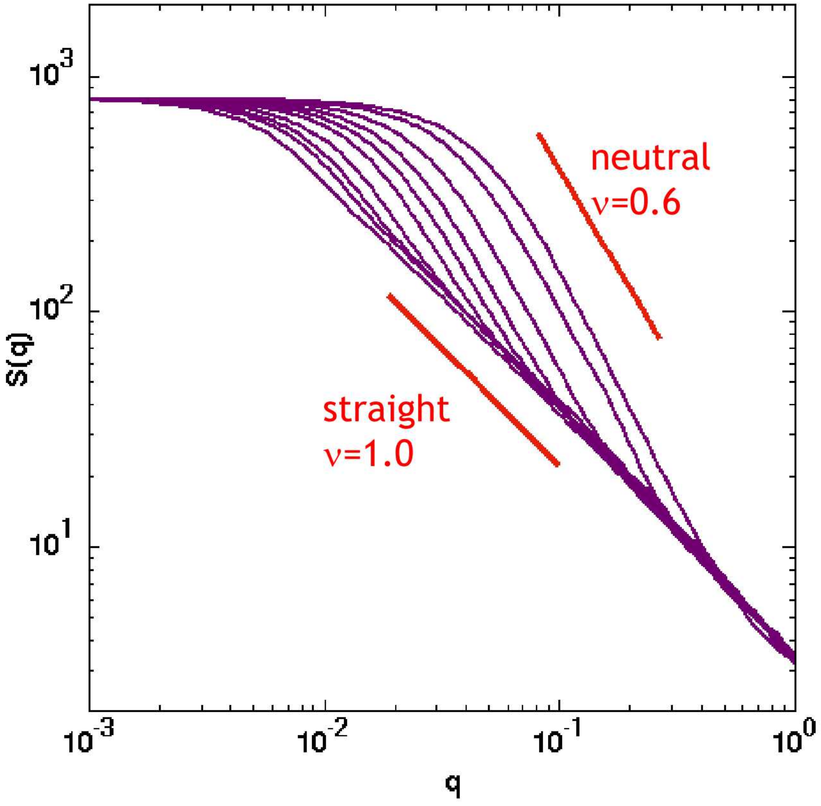
Rodlike for lengths $\ell < L_t$

L_t increases as ρ decreases

Local Chain Structure

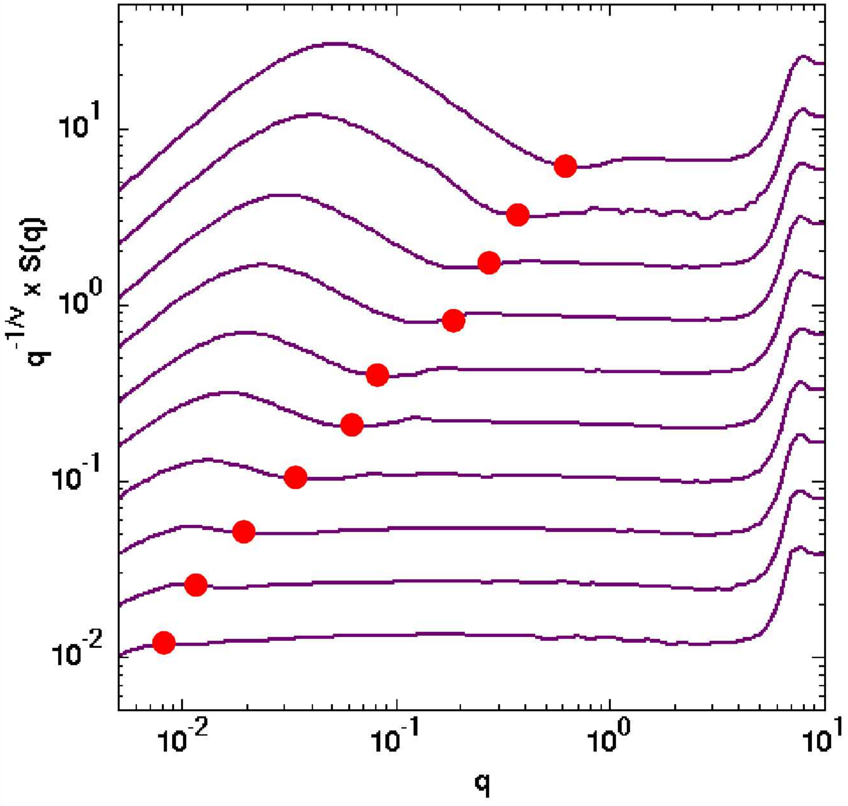
Single chain structure factor S(q)
N=800
density dependence

$S(q) \sim q^{1/\nu}$



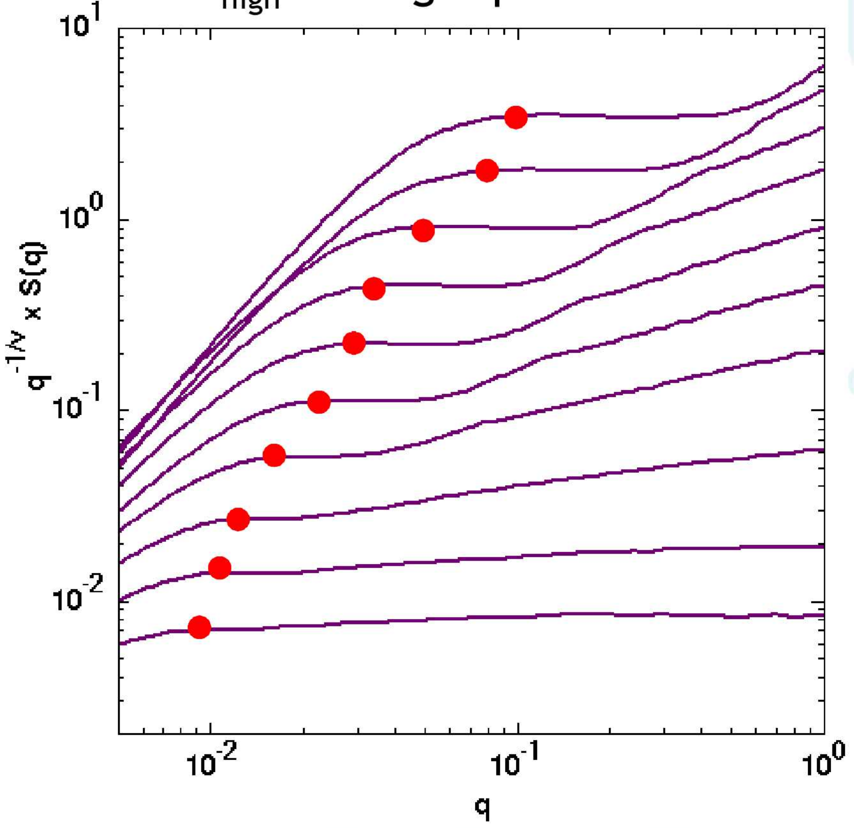
Two q-dependences (high/low)
$q_r = 2\pi/L_r$ is transition point
L_r is the ~straight segment length

ν_{low} for low q

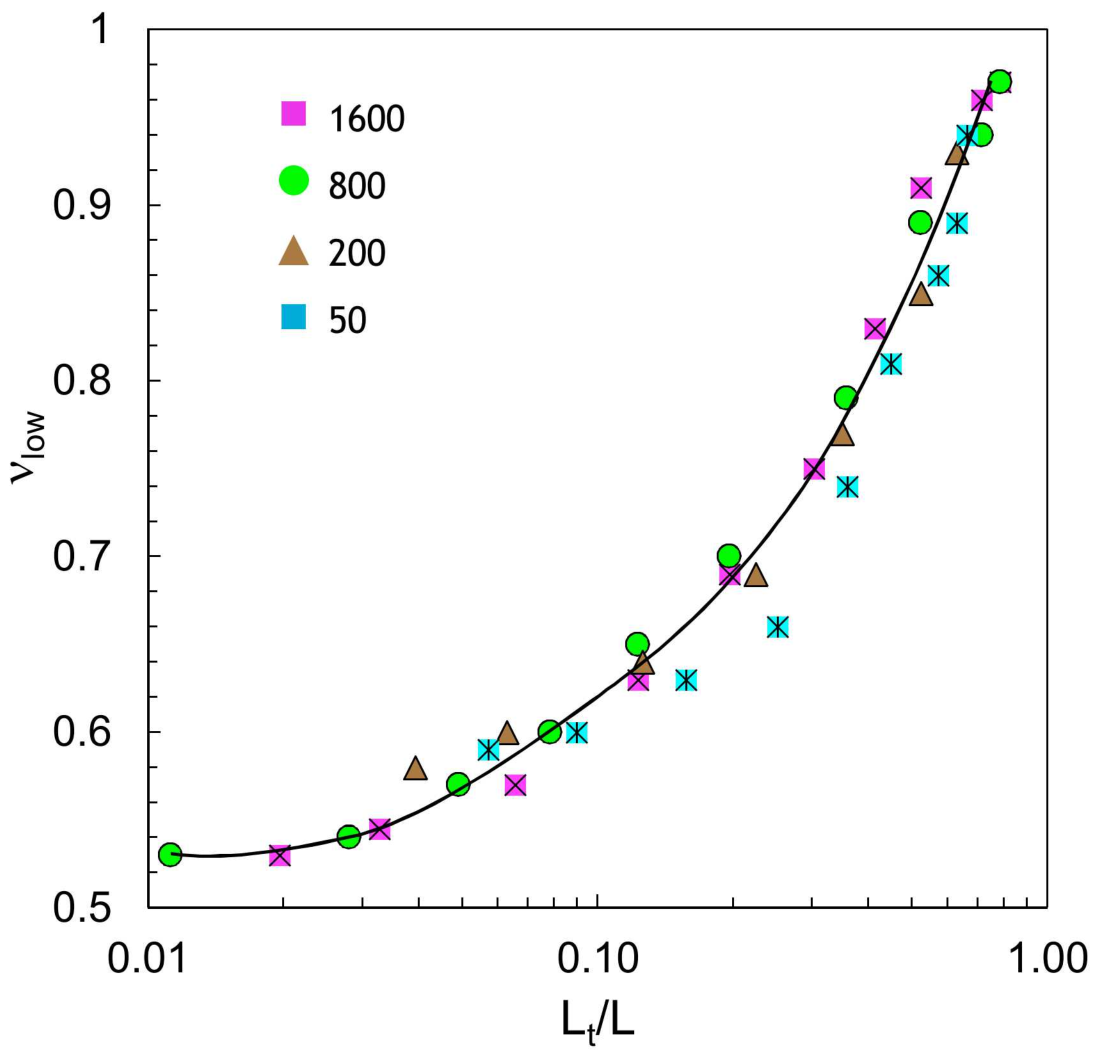


Chain is composed of ~straight segments that form a directed walk.

ν_{high} for high q



Large length scale behavior

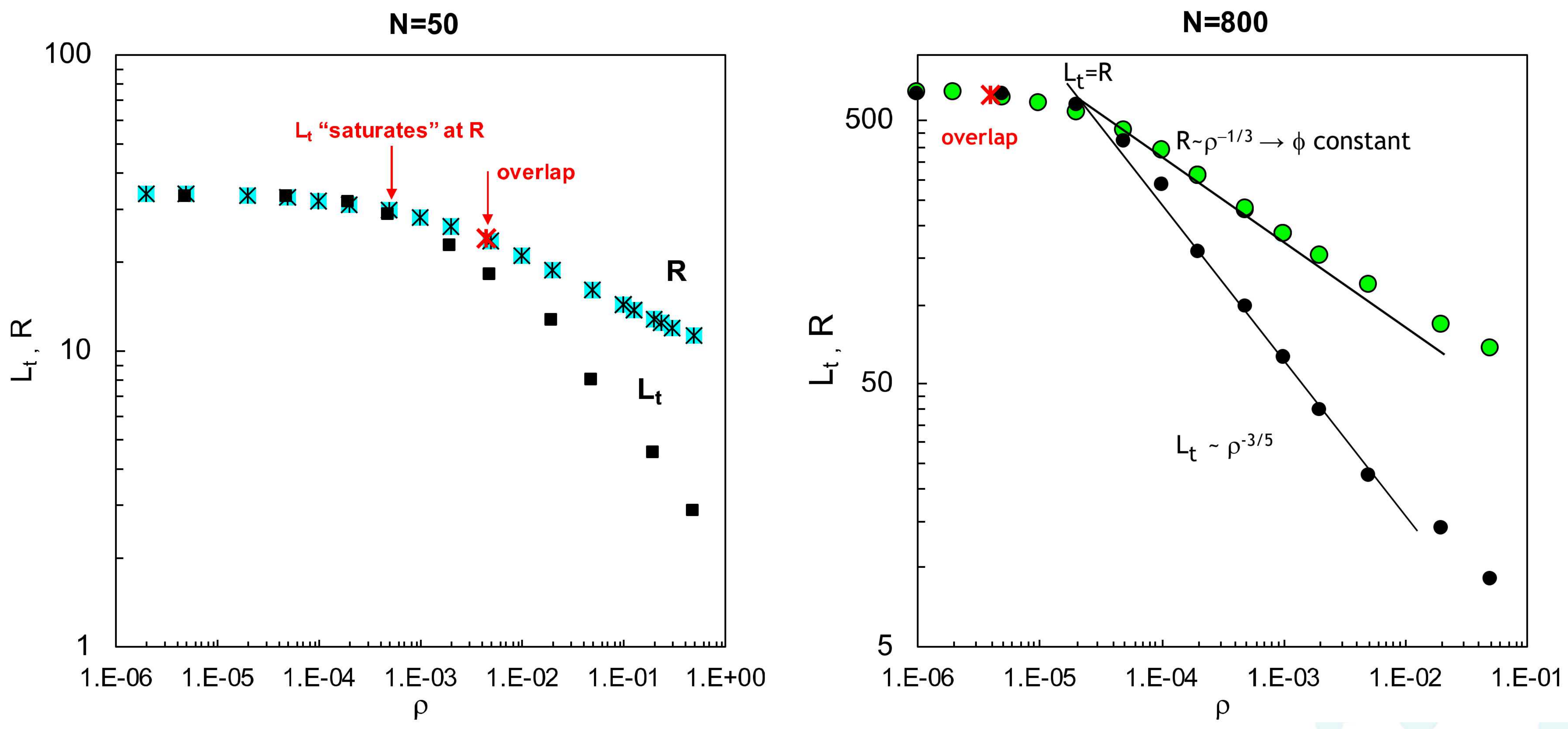


Transition from random walk at high density
  to directed walk
  just straight segment at large enough N

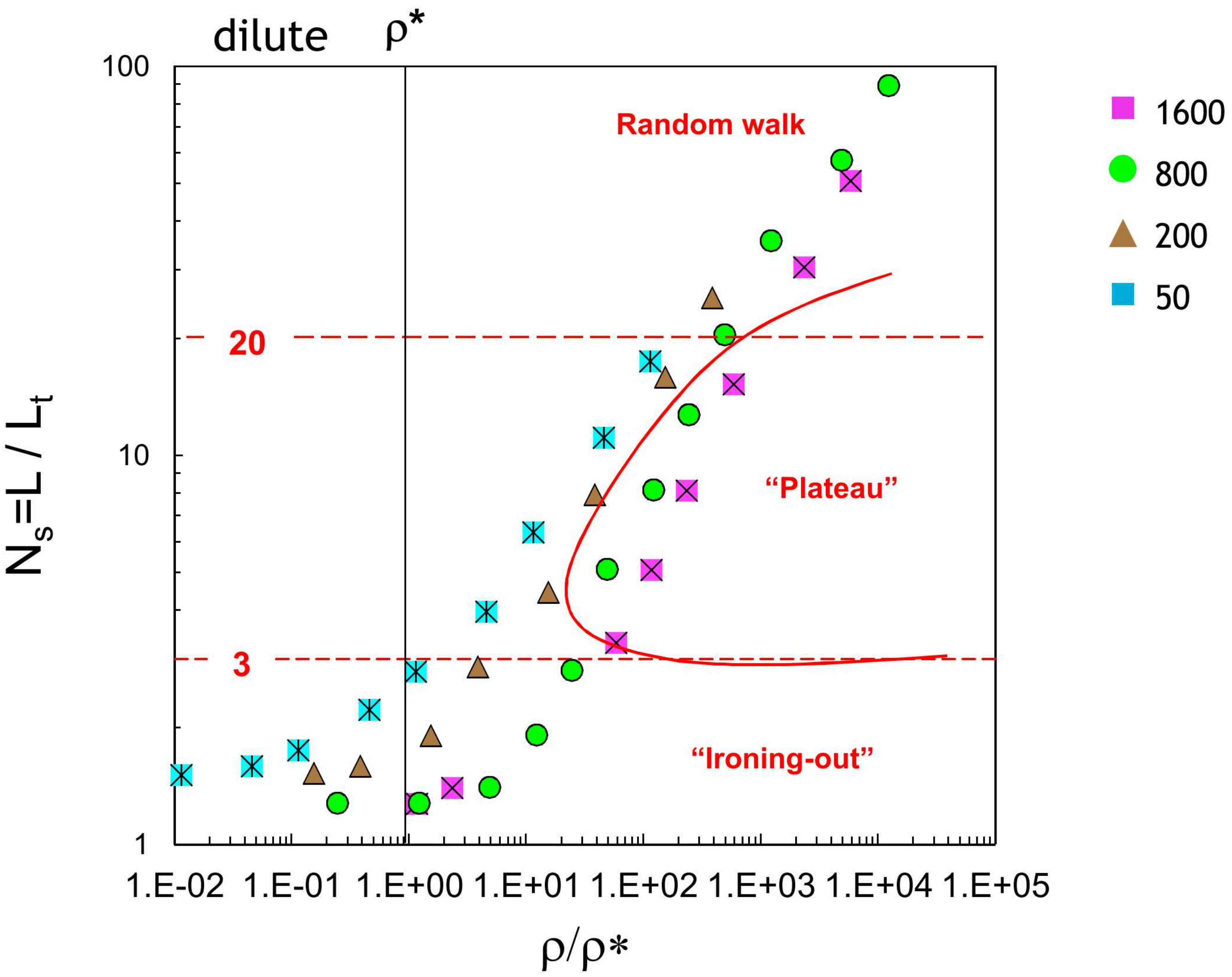
Maybe at large N (≳ 800) overlapping behavior?

ν_{high} starts at 0.90 and goes to 0.97

Segment length L_t as a function of density



Density Dependence: Number of Segments



Summary

Extended simulations out to much larger N (1600) and very much lower ρ

Find $c^* \sim N^{-2.5}$ over the range of N

reaching the unscreened dilute limit

at very large N (= 800)

shouldn't have expected N^{-2}

The chain structure at c* varies significantly.

For N ≥ 800, chains are 'fully' stretched at c*

$S(q) \sim q^{-1/\nu}$ with $\nu = 0.95+$

Density dependence of chain structure

Two regimes: straight segments and directed walk

Straight segment length increases with decreasing density

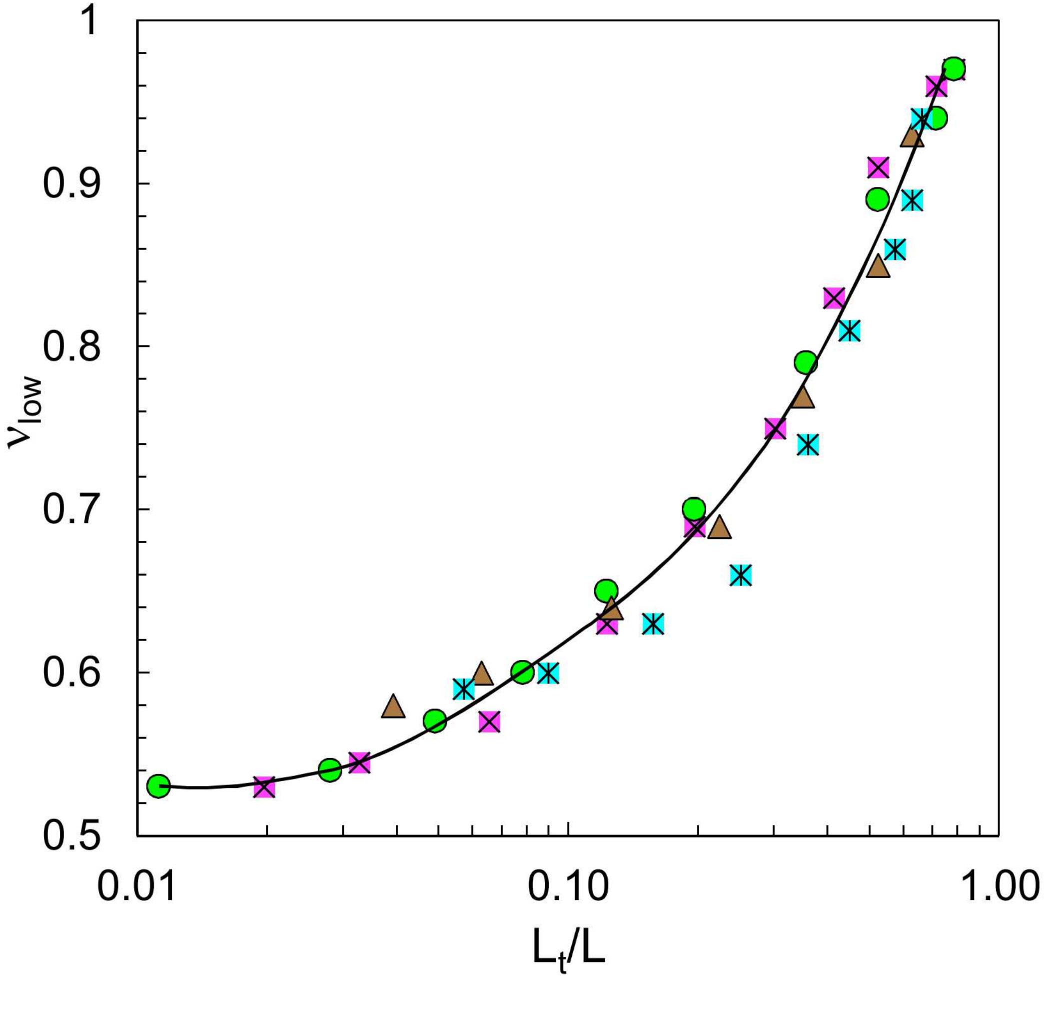
Results imply simple description possible

Need better experimental data for c*

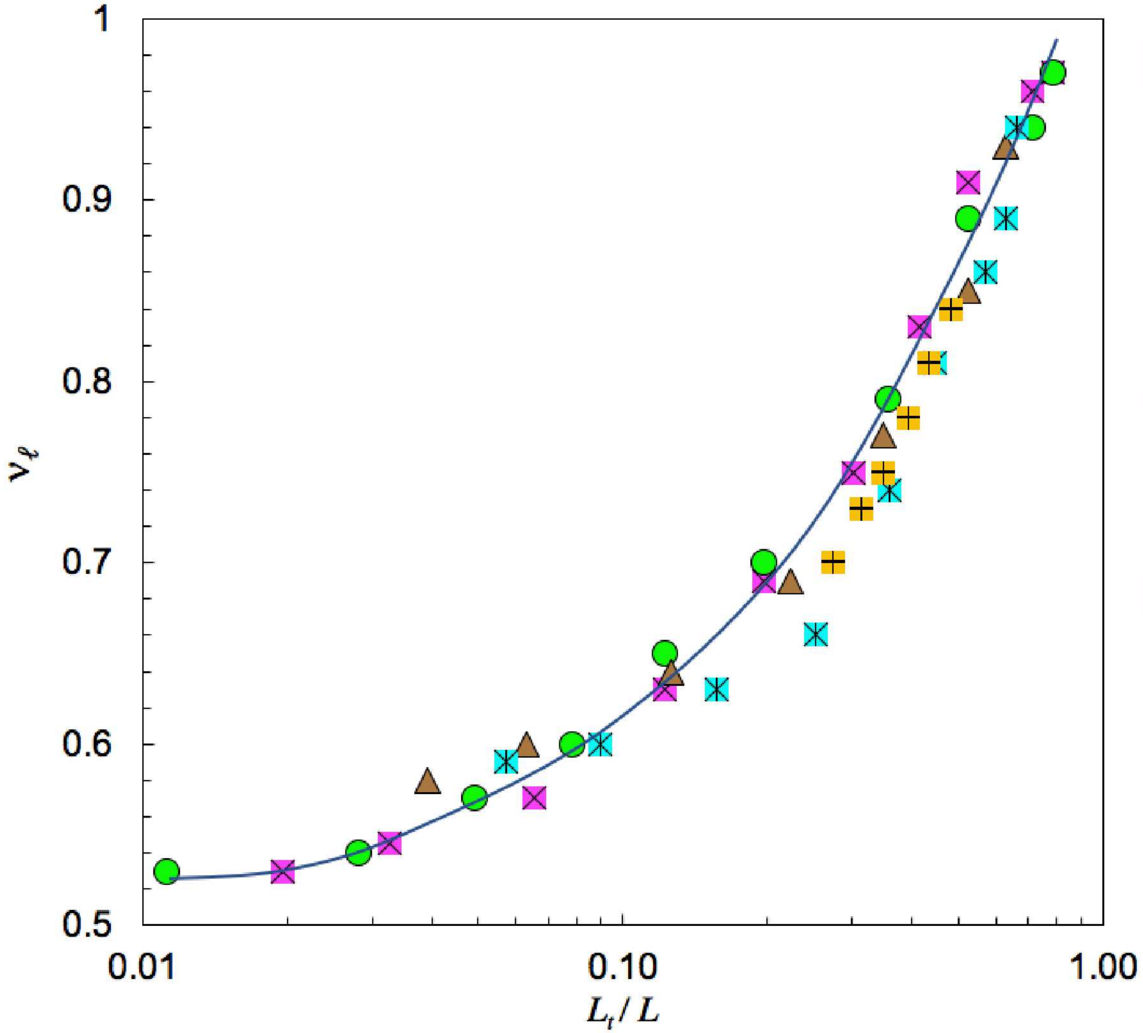
As always would like larger N for simulations

The Collaboration

Jon Bollinger, SNL
Gary Grest, SNL
Michael Rubinstein, Duke



1
0.9
0.8
0.7
0.6
0.5
0.01
0.10
1.00
L_t/L
ν_{low}



1
0.9
0.8
0.7
0.6
0.5
0.01
0.10
1.00
L_t / L
ν_ℓ