SAND2022-2519C

Overlap Concentration of Sodium Polystyrene Sulfonate in Solution

Bryce Thurston, Gary Grest, Mark Stevens,
Sandia National Laboratories

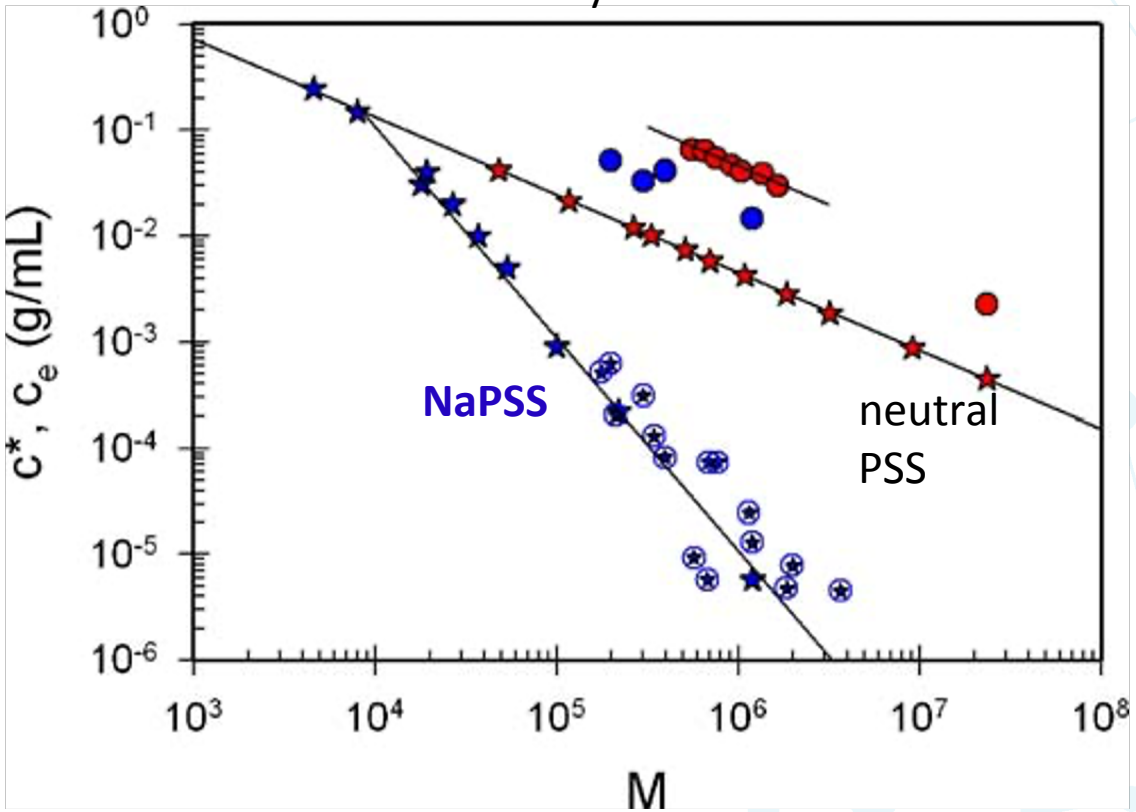
This work was performed, in part, at the Center for Integrated Nanotechnologies, an Office of Science User Facility operated for the U.S. Department of Energy (DOE) Office of Science. Sandia National Laboratories is a multi-mission laboratory managed and operated by National Technology and Engineering Solutions of Sandia, LLC., a wholly owned subsidiary of Honeywell International, Inc., for the U.S. Department of Energy's National Nuclear Security Administration under contract DE-NA0003525.

Overlap Concentration in NaPSS

NaPSS is commonly studied strongly charged polyelectrolyte.

Goal:
Do *atomistic* MD simulations of NaPSS to calculate overlap concentration *c**.

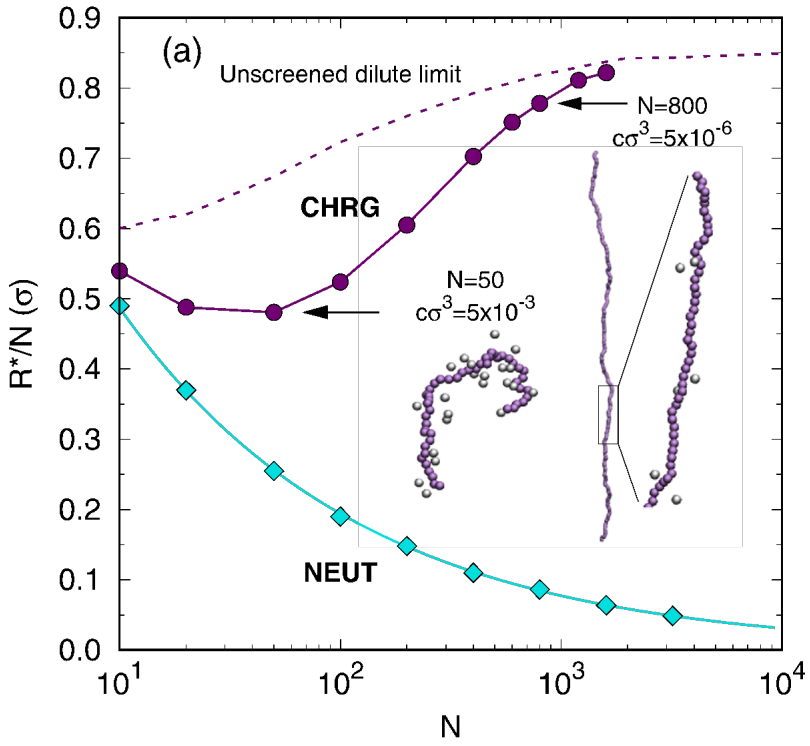
Colby 2010



Previously

Coarse-grained simulations of an ideal strongly charged polyelectrolyte with Bjerrum length = charge spacing.

R/N* reaches near 1 at about *N* = 1600.



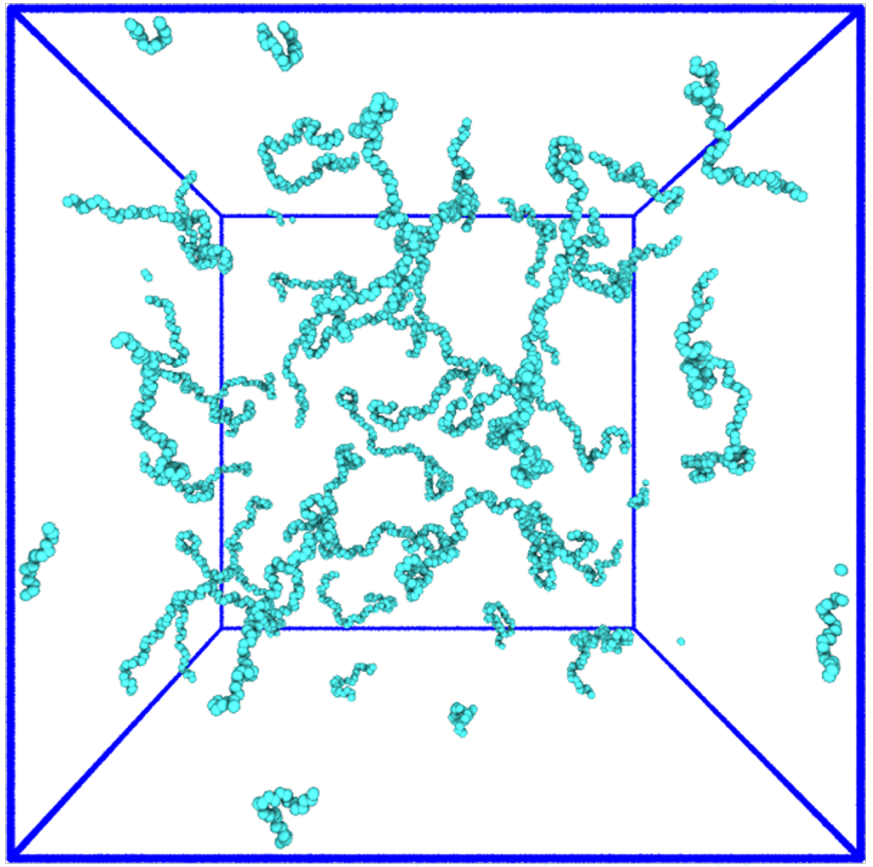
J.A. Bollinger, G.S. Grest, M.J. Stevens, M. Rubinstein, "Overlap Concentration in Salt-Free Polyelectrolyte Solutions," Macromolecules **54,** 10068-10073 (2021).

Atomistic MD simulations

Sodium Polystyrene Sulfonate (NaPSS)

- salt free systems
- number of monomers per chain *N* = 32, 64, 128 and 192
- number of chains *M* = 27
- atactic
- TIP4P-2005 water model
- L-OPLS force-field
- run time 4 μs for *N* = 32; 500 ns for *N*=192
- calculate overlap concentration c*
- and end-to-end distance *R**
  - volume fraction ϕ is random close packed at c*.

$$\phi^* = \frac{\pi}{6V}\sum_i \langle R_i^3 \rangle = 0.64$$



27 chains of N=64 at c=0.098 g/mL
water and Na not shown

Coarse-grained simulations

Standard bead-spring model

- every monomer charged
  - charge separation = 2.82 Å
  - Bjerrum length = 7.1Å
- number of monomers per chain *N*: 32—1200
- number of chains ≥ 32

Match atomistic data:
Hydrophobic backbone-backbone interactions are essential.
Add attractive part of LJ between monomers
ε_{mm} = 2.0 and cutoff = 2.5 σ

(other LJ interactions are purely repulsive and ε=1)

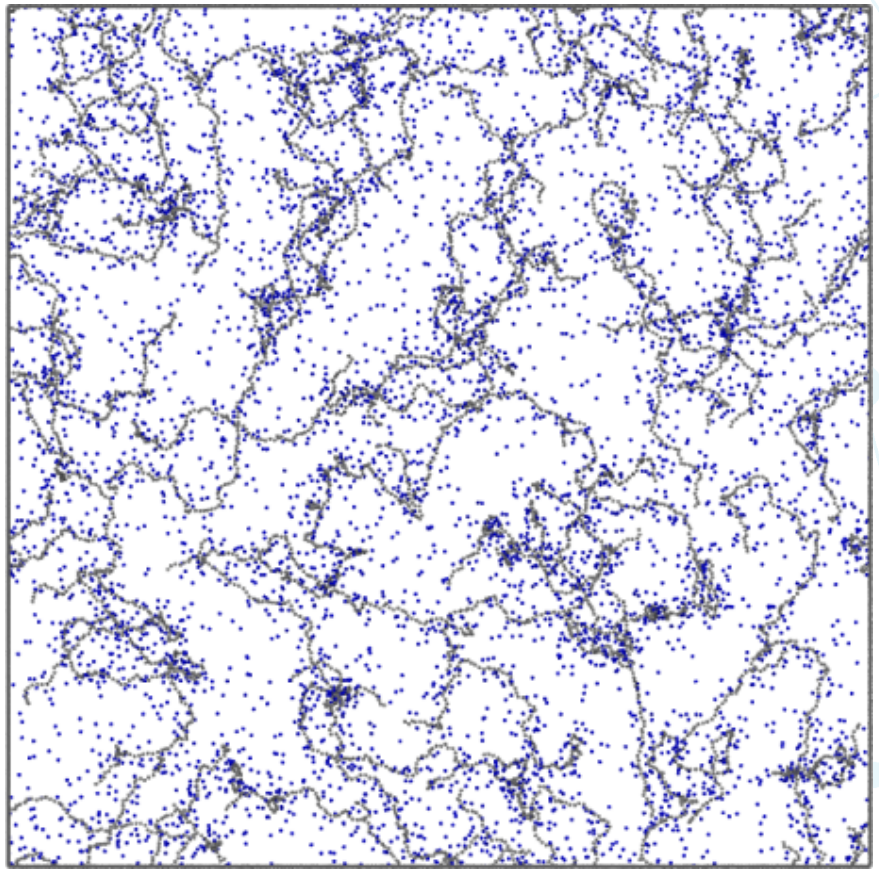
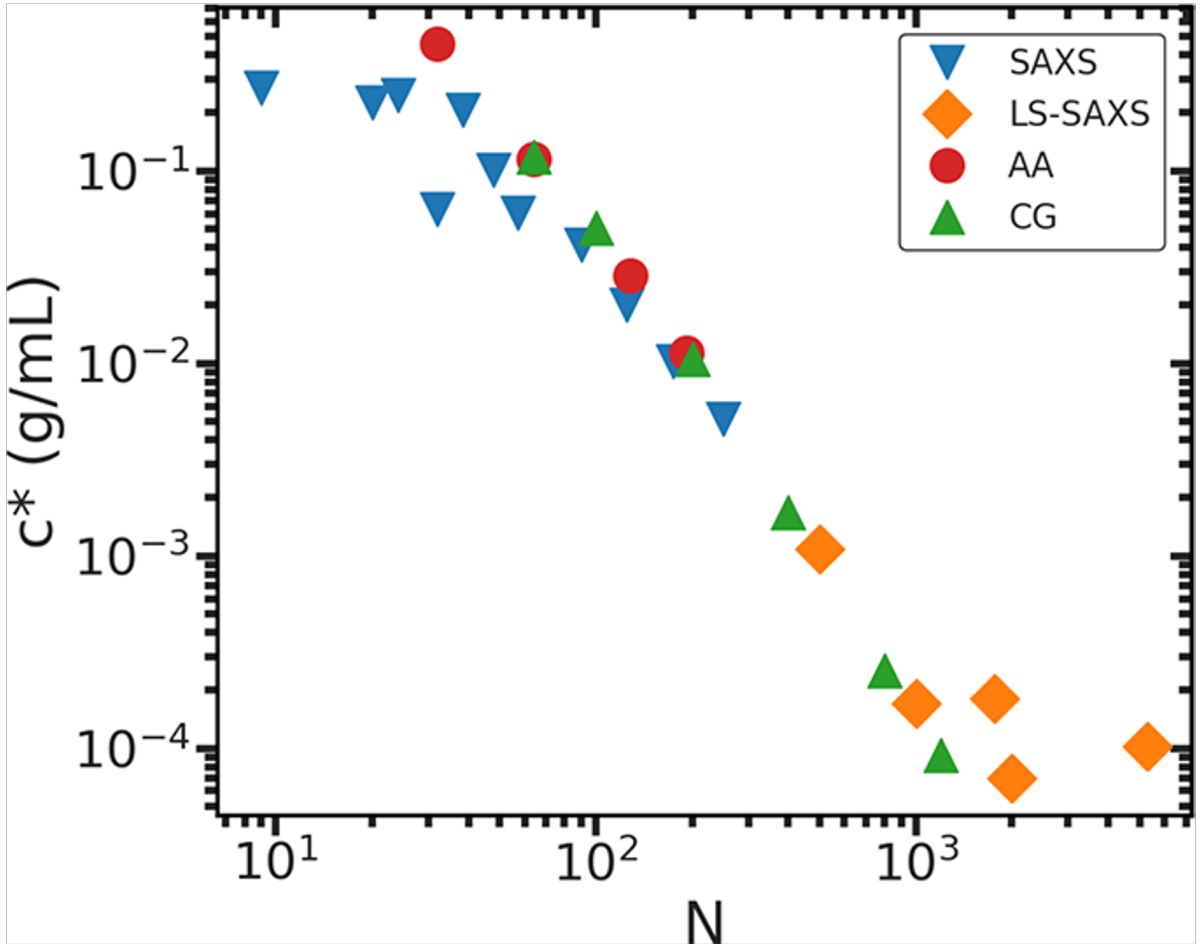


Image of CG system

Comparison to Experimental Data

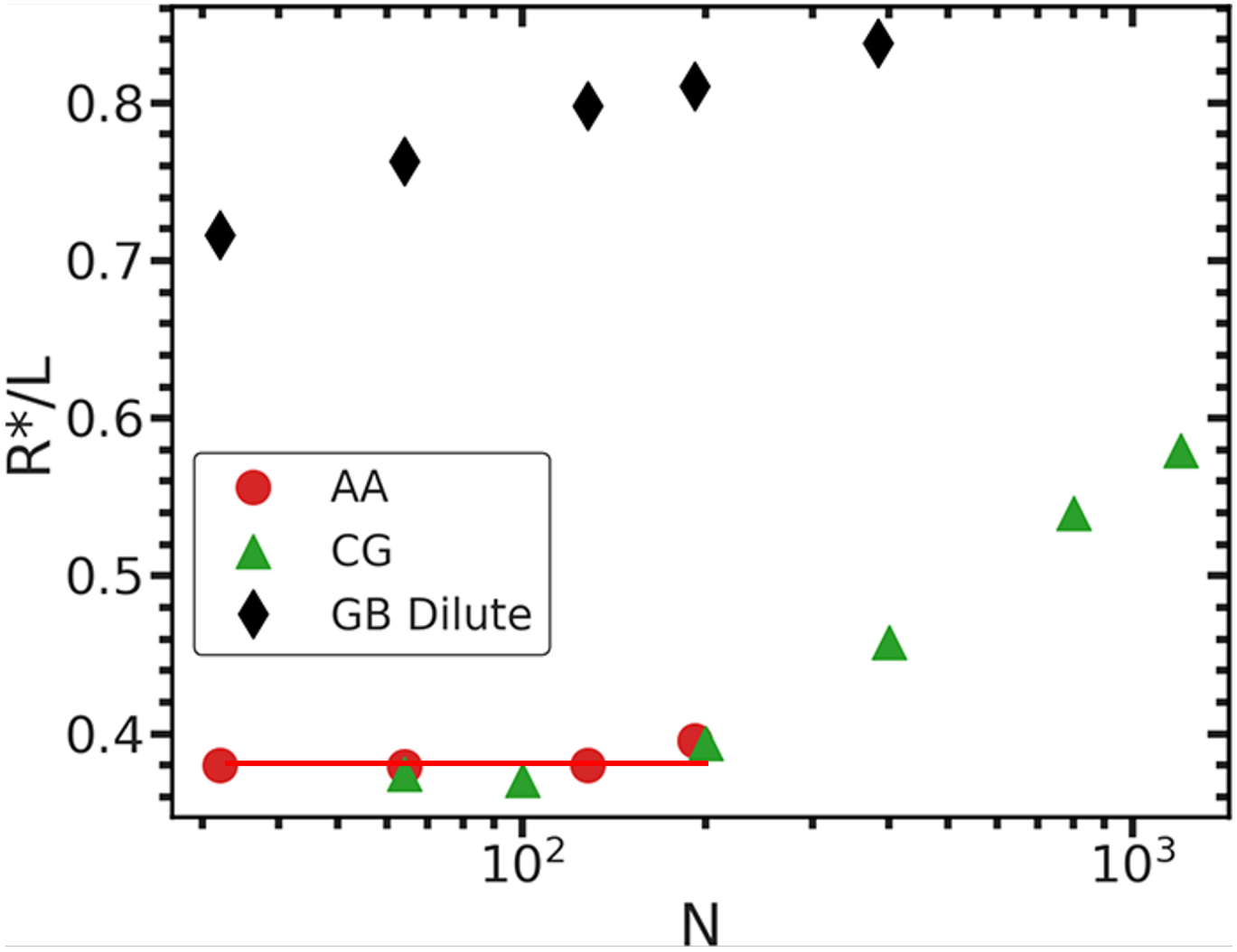


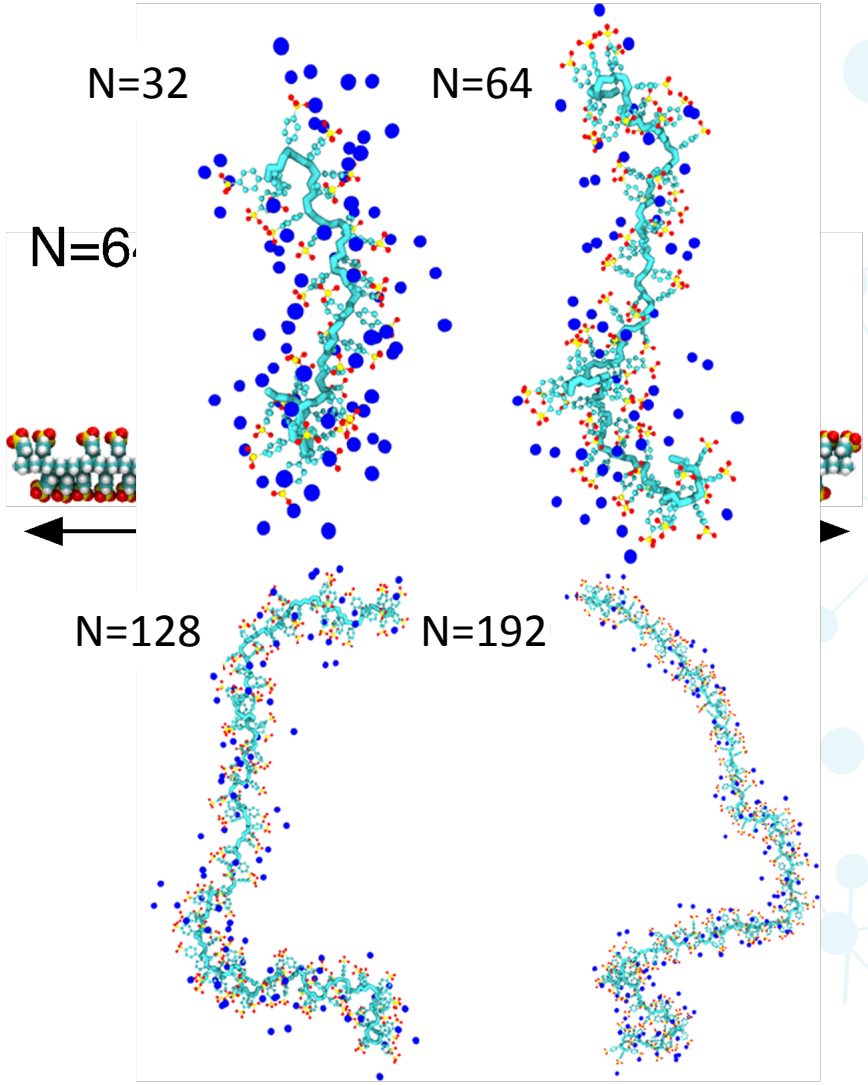
scattering data

AA = all atom (atomistic MD)

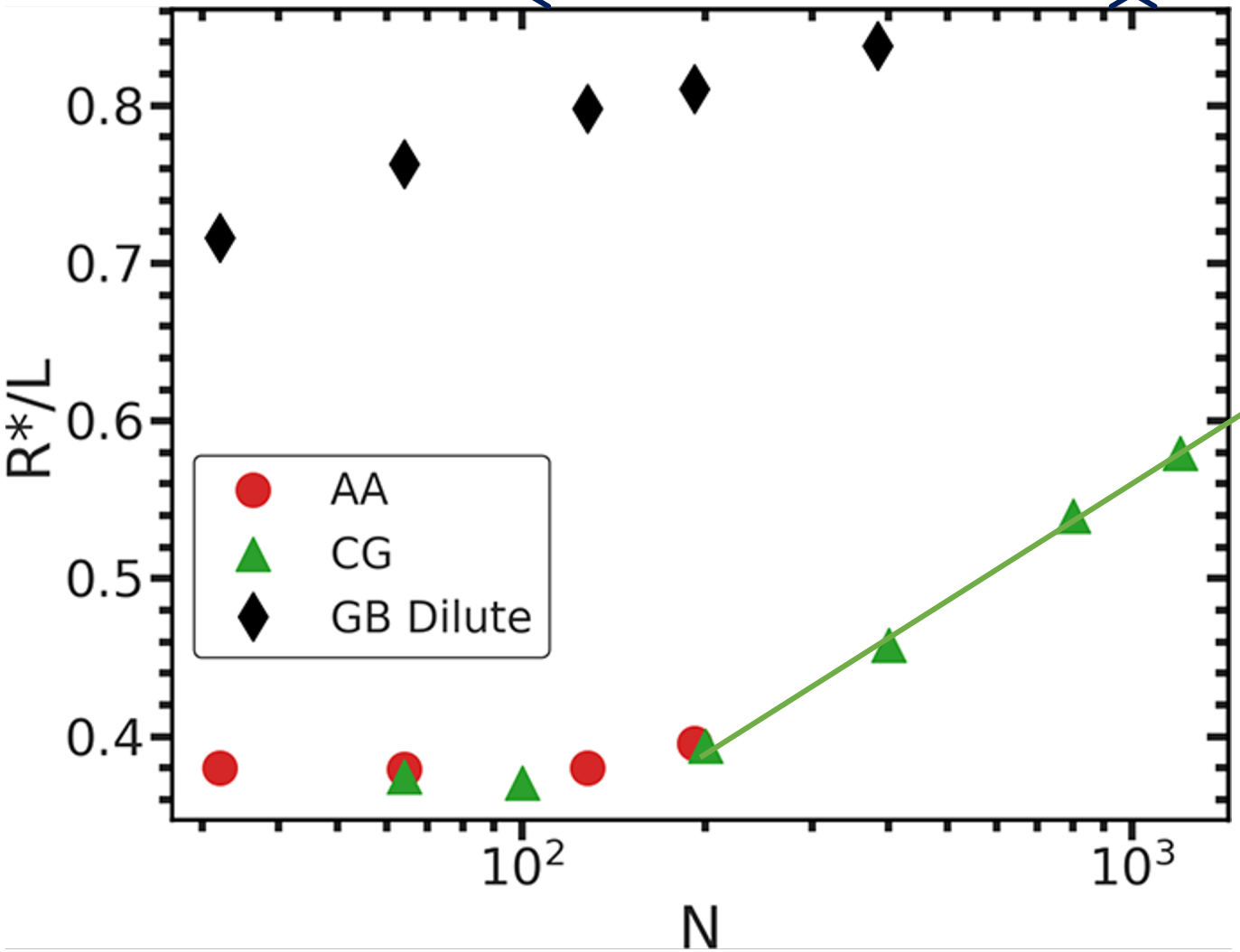
CG = coarse-grained MD

Chain Size at Overlap



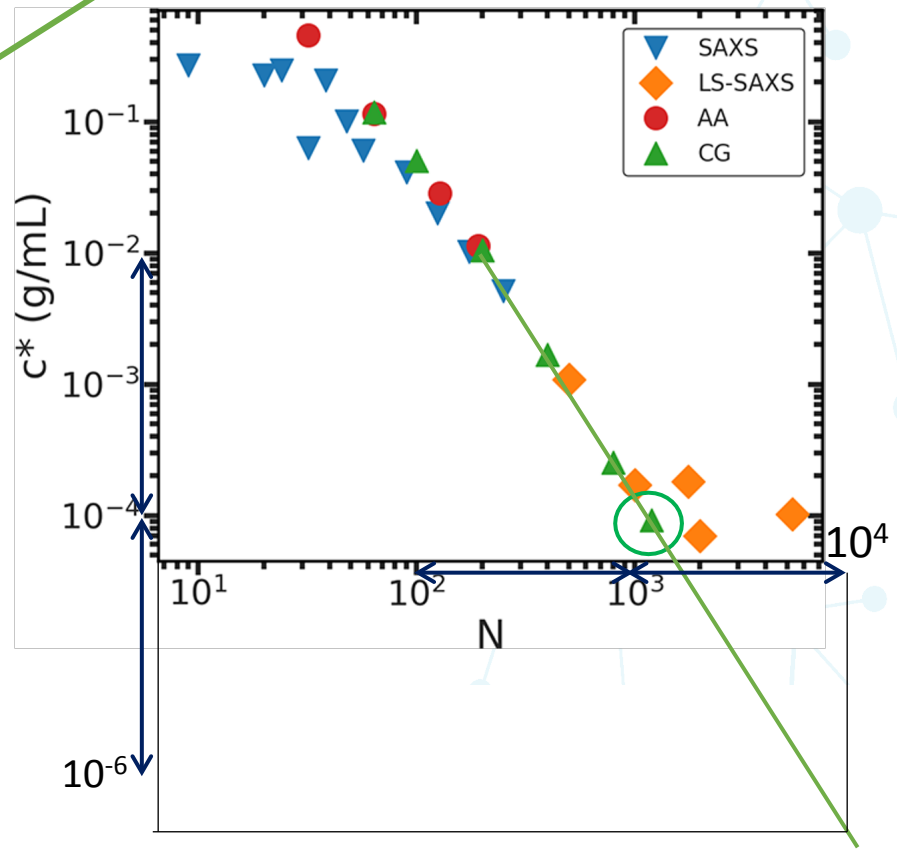


Where does large N limit start?



10^4

$c^* < 10^{-6}$ g/mL $> 10^4$

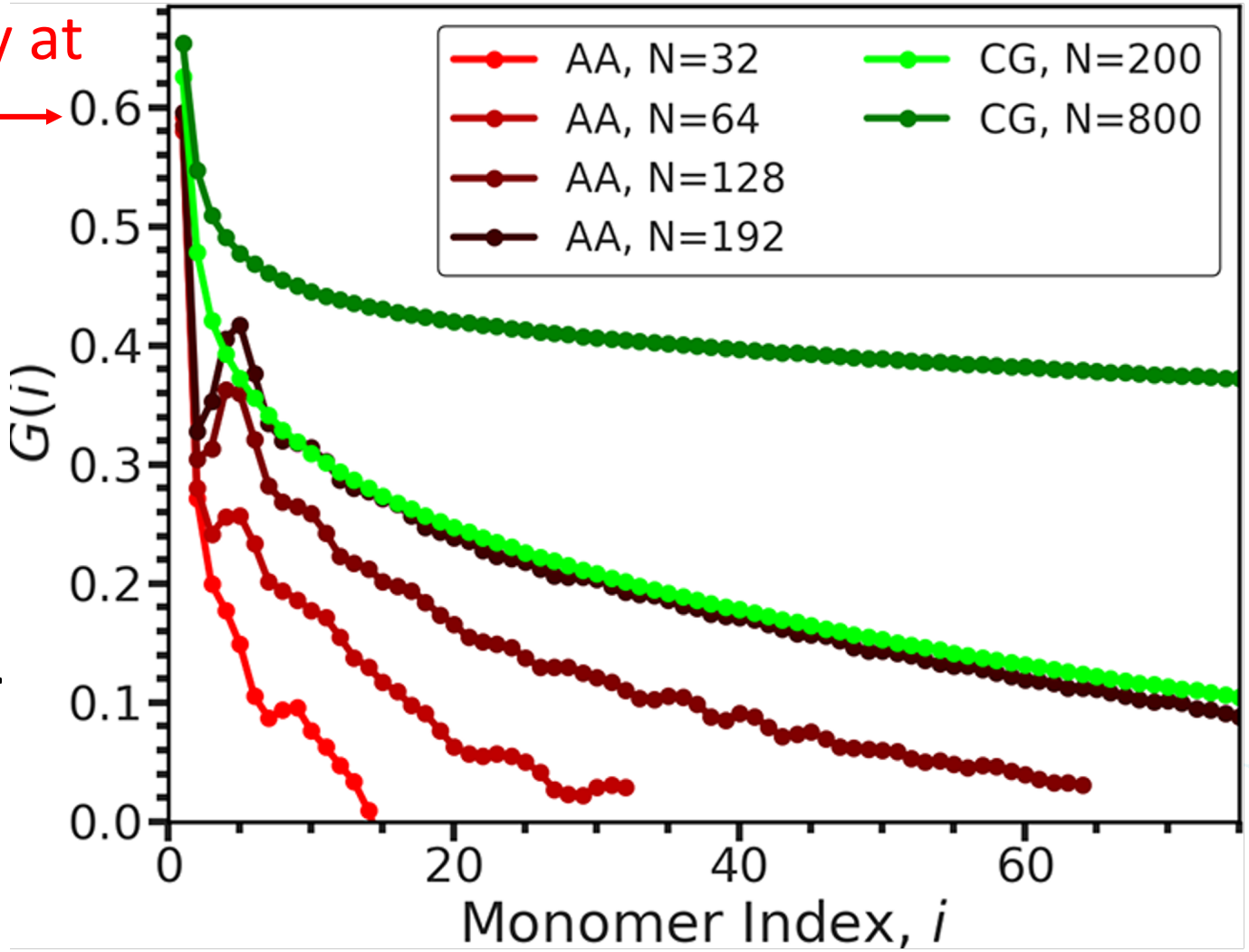


Tangent Correlation: Flexible Chains

Drops precipitiously at small i →

$G(i) = \langle \hat{r}_{j+i} \cdot \hat{r}_j \rangle$

r is the vector from monomer j to j+1



$G(i) \sim e^{-r/L_p}$

L_p is persistence length.

Atomistic simulations find Na PSS does follow this wormlike chain model.

Conclusions

Performed **multichain atomistic** simulations of **NaPSS** at N=32 to 192
Developed matching coarse-grained model enabling simulations to N=1200
Hydrophobic interactions are noticeable in NaPSS

R*/L = 0.38 for the atomistic simulations.
At overlap the chains are not fully extended for these N.

From CG simulations, *N*=1200 is not in the scaling regime.
The scaling regime may not be practically reachable in experiments.
$N \sim 10{,}000$ and $c^* < 10^{-6}$ g/mL
Too low of a concentration at the necessary *N*.

B.A. Thurston, G.S. Great and Mark J. Stevens,
"Overlap Concentration of Sodium Polystyrene Sulfonate in Solution,"
ACS Macro Lett. **11,** 217-222 (2022).

J.A. Bollinger, G.S. Grest, M.J. Stevens, M. Rubinstein,
"Overlap Concentration in Salt-Free Polyelectrolyte Solutions,"
Macromolecules **54,** 10068-10073 (2021).

Funding & Resources:
Oak Ridge Leadership Computing Facility

DOE Office of Science, Basic Energy Sciences,
Division of Materials Sciences and Engineering