Coarse-Grained Modeling of Ionomers and Salt-Doped Block Copolymers

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Map from Wikimedia Commons

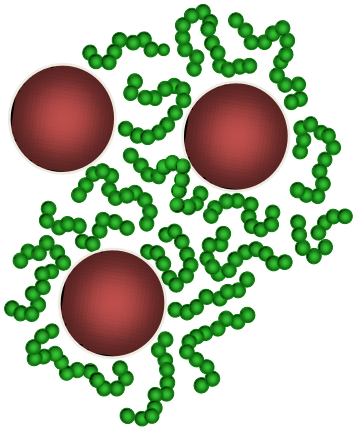
Experience

Coarse-Grained Polymers

Polymer Nanocomposites

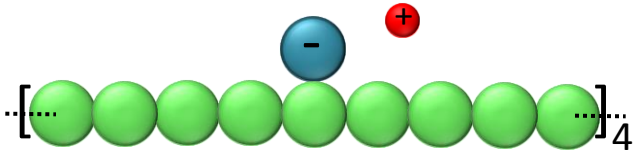
Applications: Car tires, fuel cells, photovoltaics

http://www.ppg.com/specialty/silicas/productsegments/Pages/green_tires.aspx



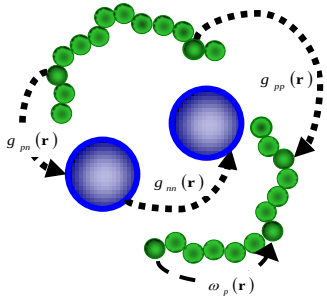
Ionomers

Applications:
Golf balls, packaging,
Battery electrolytes?

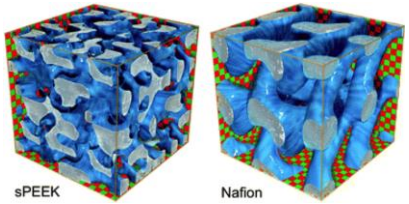


3 types of computational methods

PRISM liquid state theory

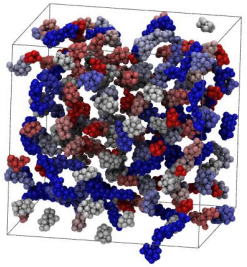


Classical fluids density functional theory



Komarov et al. Soft Matter 6, 3939 (2010)

Molecular dynamics simulations



Motivation: Understanding Ionic Aggregation in Ionomers

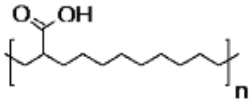
Ionomers as electrolytes

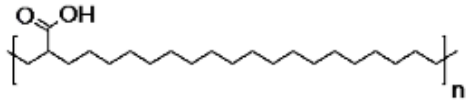
- Single ion conducting ability
- Chemically, mechanically stable
- Challenge: low ion conduction

Fundamental polymer science

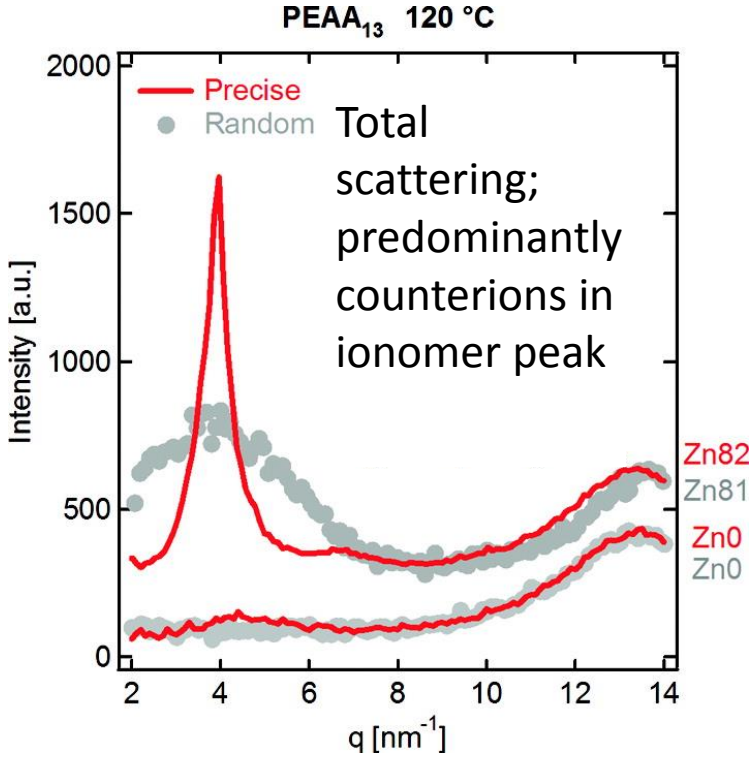
Experimental advances

- ADMET synthesis → precise spacing of acid groups (Wagener group, U Florida)





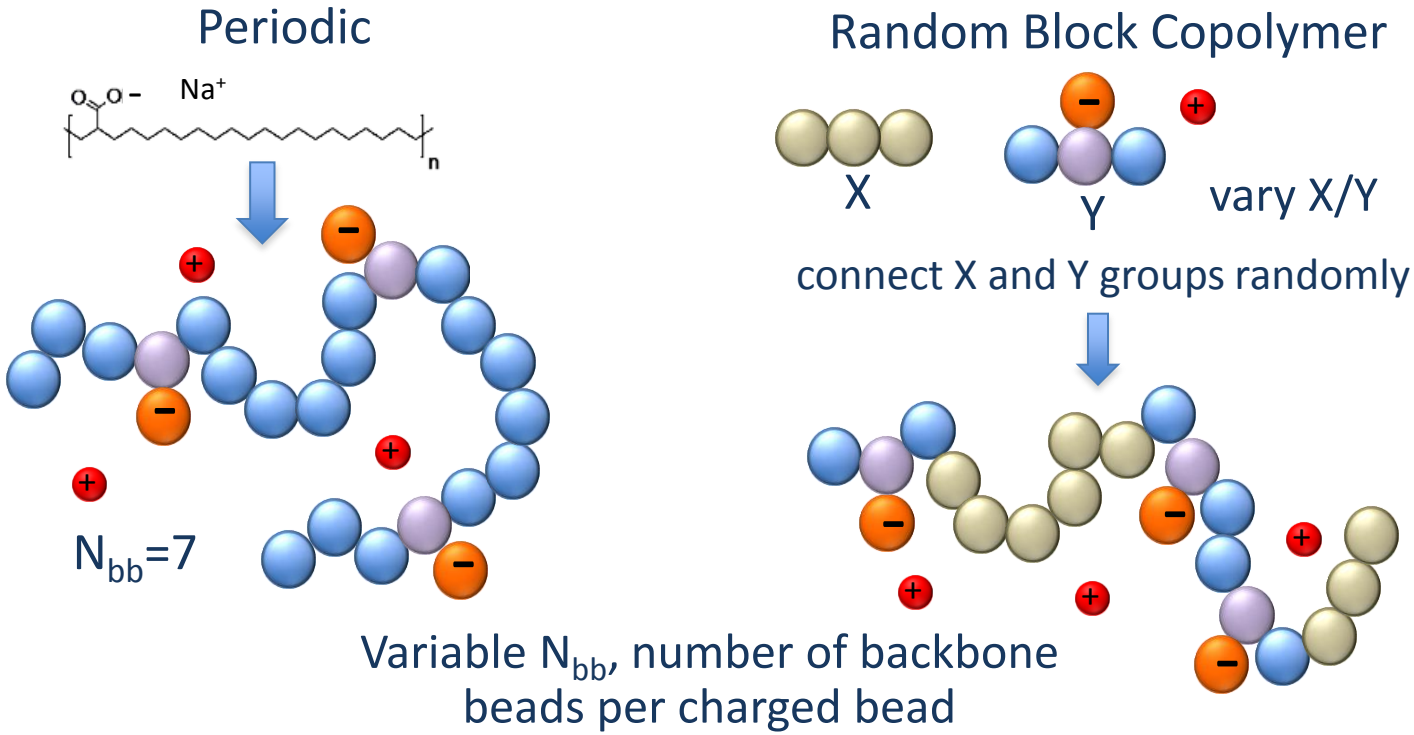
- Neutralized, characterized
- Sharp, large ionomer peak
- Ideal for comparison to MD



From: M. E. Seitz; C. D. Chan; K. L. Opper; T. W. Baughman; K. B. Wagener; K. I. Winey; *J. Am. Chem. Soc.* **2010,** 132, 8165-8174.

Coarse-Grained Molecular Dynamics Simulations of Ionomers

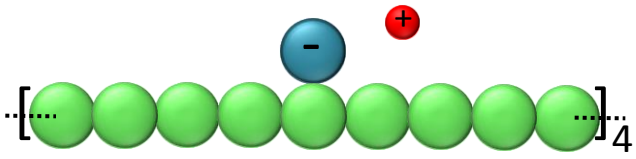
- Long time, length scales accessible
- Simple bead-spring polymer, multiple atoms represented as one bead



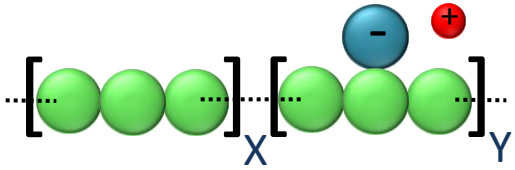
- Captures key aspects: polymer entropy, ionic interactions
- Missing: local dielectric properties, specific chemistry

Cluster Morphology

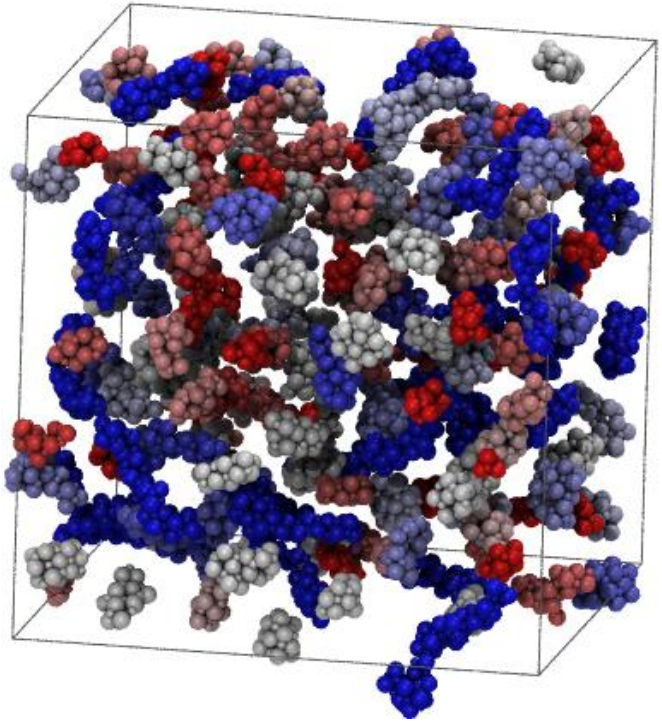
Periodic Spacing
narrow cluster size distribution
mean cluster size 31 ions

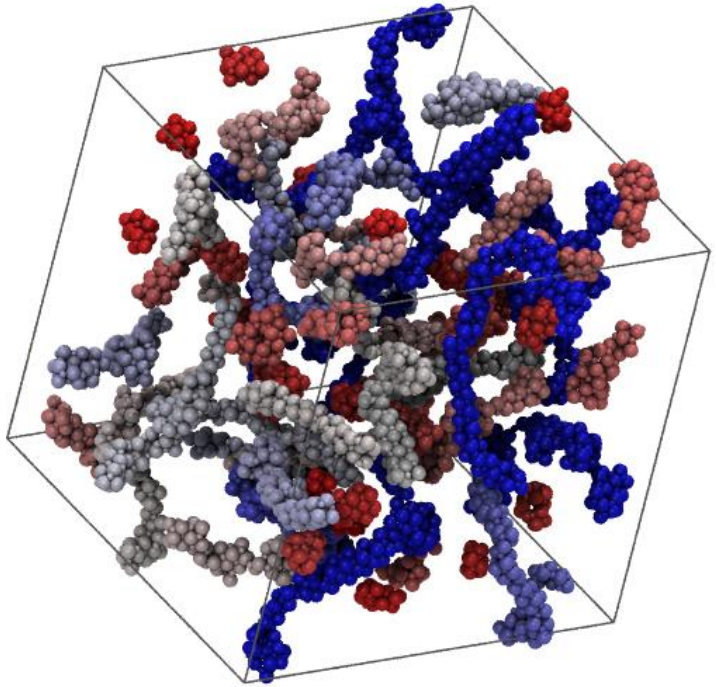


Random Block Copolymer
stringy, large clusters
mean cluster size 87 ions



X/Y=2 X+Y=12





Snapshots showing only ions, colored by cluster size

Small clusters → **Large clusters**

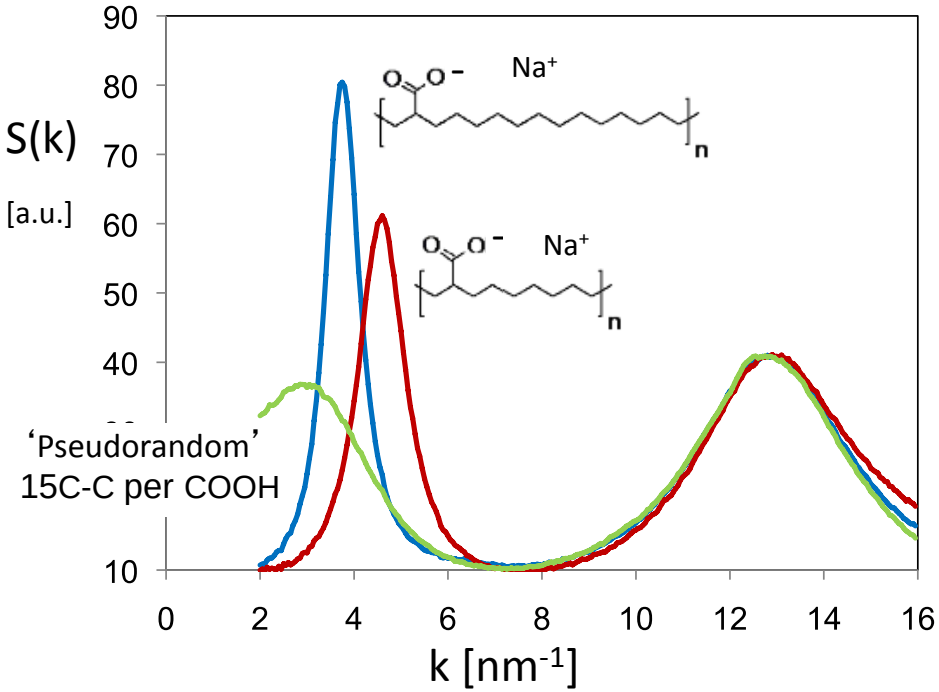
PRL 106, 127801 (2011)

background dielectric constant = 4

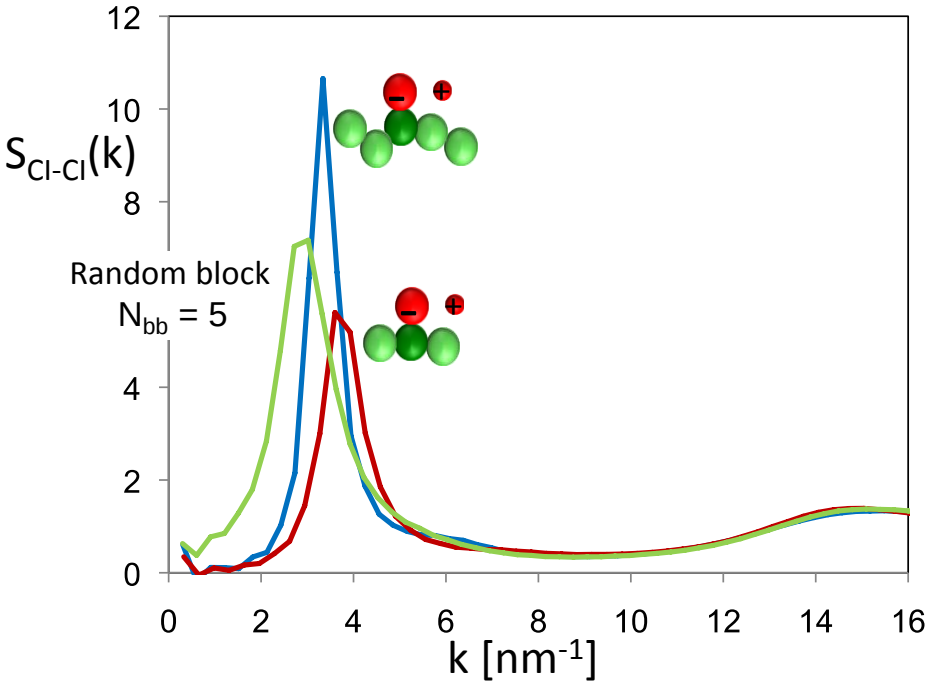
Comparison to Experimental Scattering

- Increasing spacing moves ionomer peak to lower wavevector for both experimental data and simulated counterion-counterion structure factor
- Random block copolymer architecture similar to experimental pseudorandom: broader, lower wavevector peak (larger aggregates of more variable size)
- Experiments: 28-34% neutralized, simulations: fully neutralized

Experiment



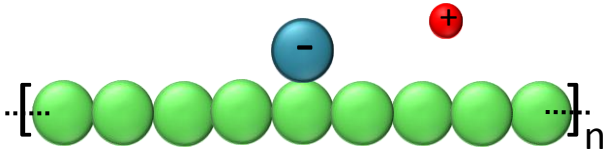
Simulation

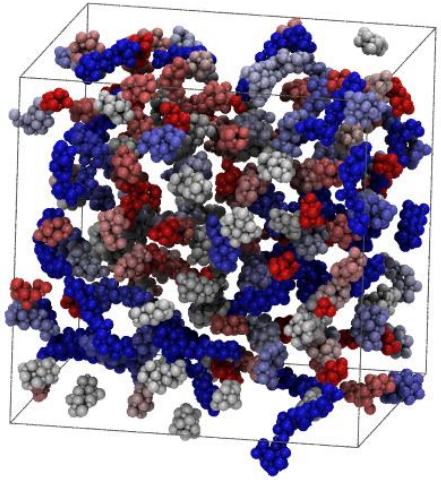


Details in Hall, Seitz et al. *JACS* 134, 547-587 (2012)

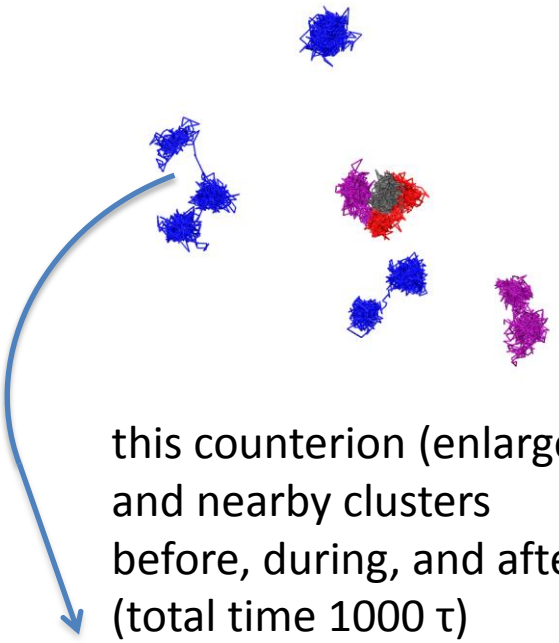
Ion trajectories appear to "hop"

But mechanism is not standard hopping

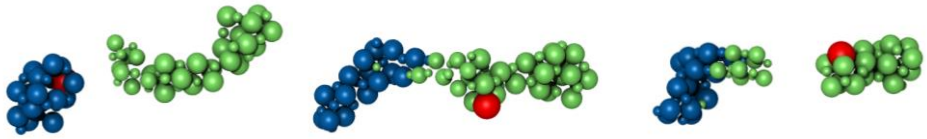




4 counterion trajectories (blue)
and 3 anion trajectories
(red and purple on one polymer,
polymer center of mass in grey,
another anion in purple)
1000 steps of 50 τ each



this counterion (enlarged in red)
and nearby clusters
before, during, and after its "hop"
(total time 1000 τ)

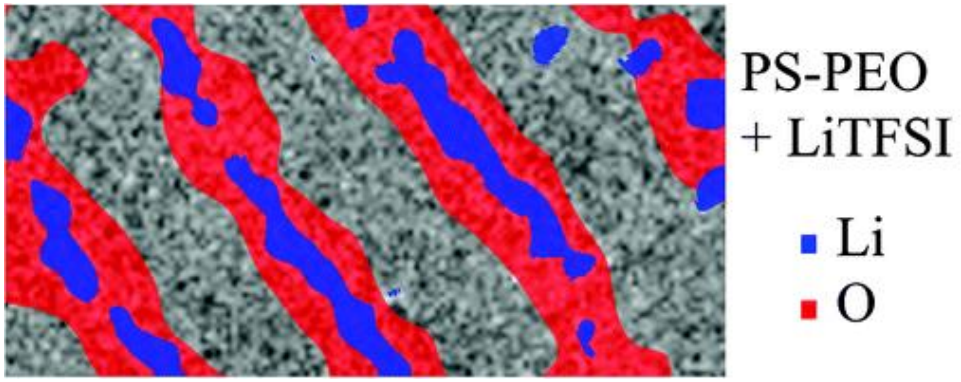


Salt-Doped Block Copolymers for Batteries

- High modulus, nonflammable battery electrolytes can allow the use of solid lithium electrode (lightweight)
- Two unlike polymers connected into the same molecule can microphase separate into various ordered phases
- Ions contained in one phase that conducts, other phase gives desired material properties
- Balsara group studies lamellar PS-PEO with Li salts; works well at controlled temperature

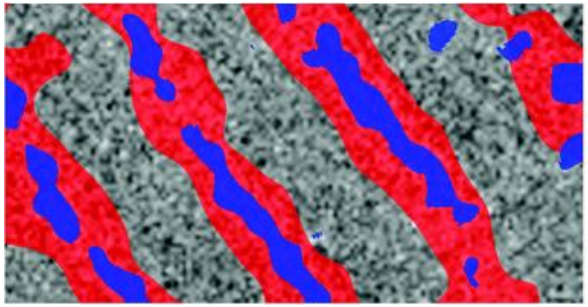
Energy-filtered TEM image:
Li salt is primarily in PEO block

From E.D. Gomez *et al. Nano Letters* **9**, 1212-1216 (2009).



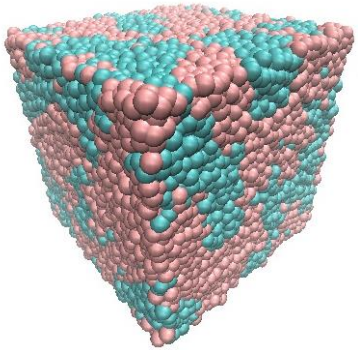
Salt-Doped Block Copolymers

- Why coarse-grained simulations
  - Many parameters, not clear how to optimize without fundamental understanding
  - Need charges, long time and length scales



From E.D. Gomez *et al. Nano Letters* **9**, 1212-1216 (2009).

Equilibration is hard:



Diblock copolymer melt $N_A=N_B=20$ $\varepsilon_{AB}=1.9$

at $\tau_{LJ}=1{,}000{,}000$ after starting from random configuration

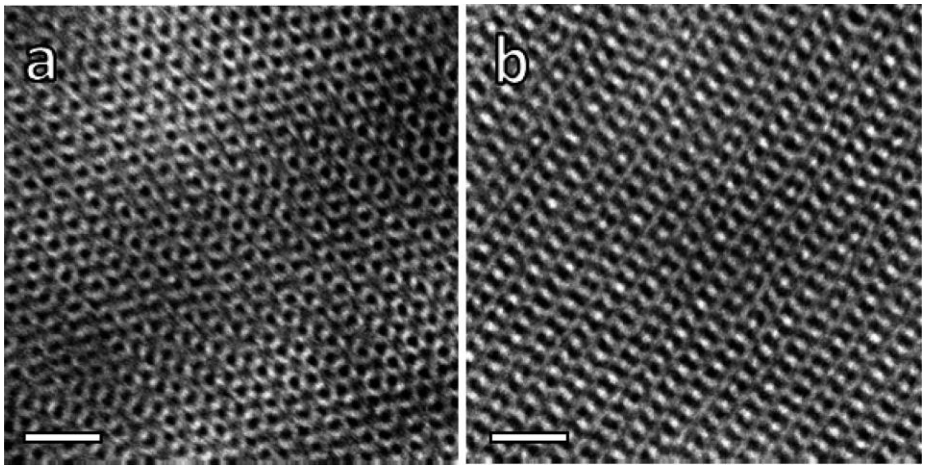
- Options to equilibrate MD simulations of block copolymers
  - Use Monte Carlo moves (ions add complications)
  - Start from close to equilibrated structure (must know equilibrated structure)
- New strategy
  - Simple model; maps nicely between MD and fluids density functional theory
  - Start MD simulations using morphology information from fDFT
  - fDFT is also fast (helps search parameter space), gets free energies

Tapered Block Copolymer Motivation

Want gyroid phase at high MW; need additional tunable parameter

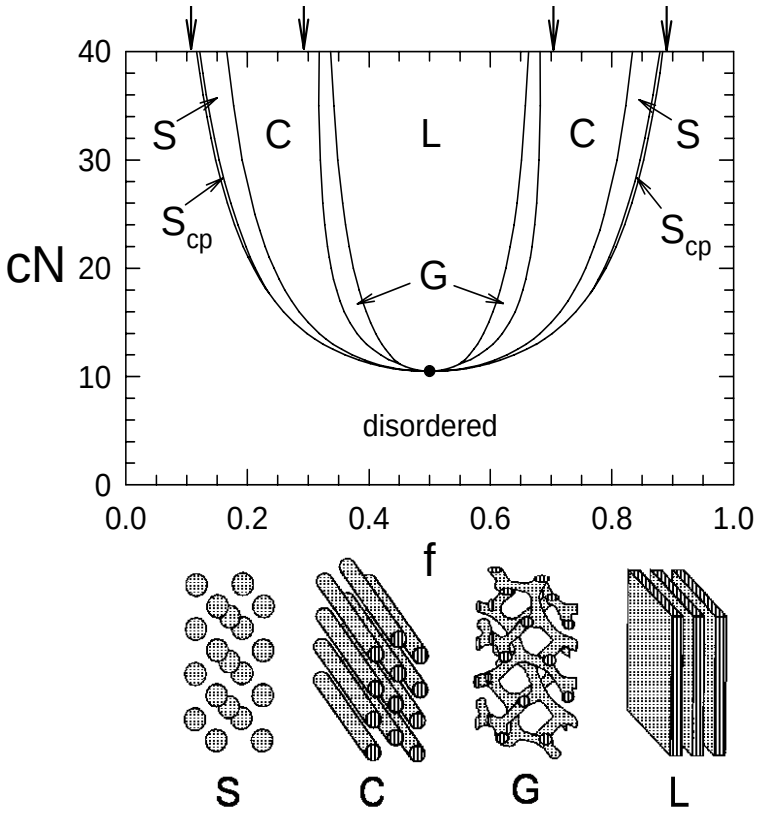
Tapered diblock systems

Still shows gyroid phase



Roy, R. et al. Macromolecules 44, 3910–3915 (2011).

Diblock SCFT phase diagram



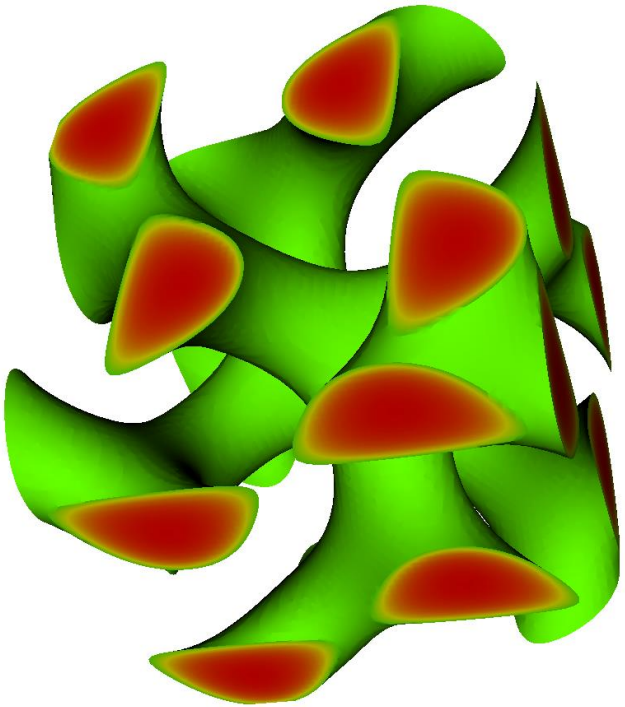
What do the SCFT phase diagrams look like for these systems?

Matsen, M. W.in *Soft Matter* (Gompper, G. & Schick, M.) 87–178 (Wiley-VCH Verlag GmbH & Co. KGaA, 2007)

Methodology

Self-Consistent Field Theory (SCFT)

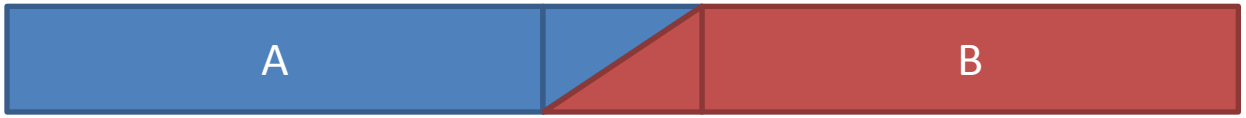
- PolySwift++ by Tech-X Corporation
- Incompressible Gaussian chains
- A and B type monomers identical
- Phase diagrams (S/C/G/L only)

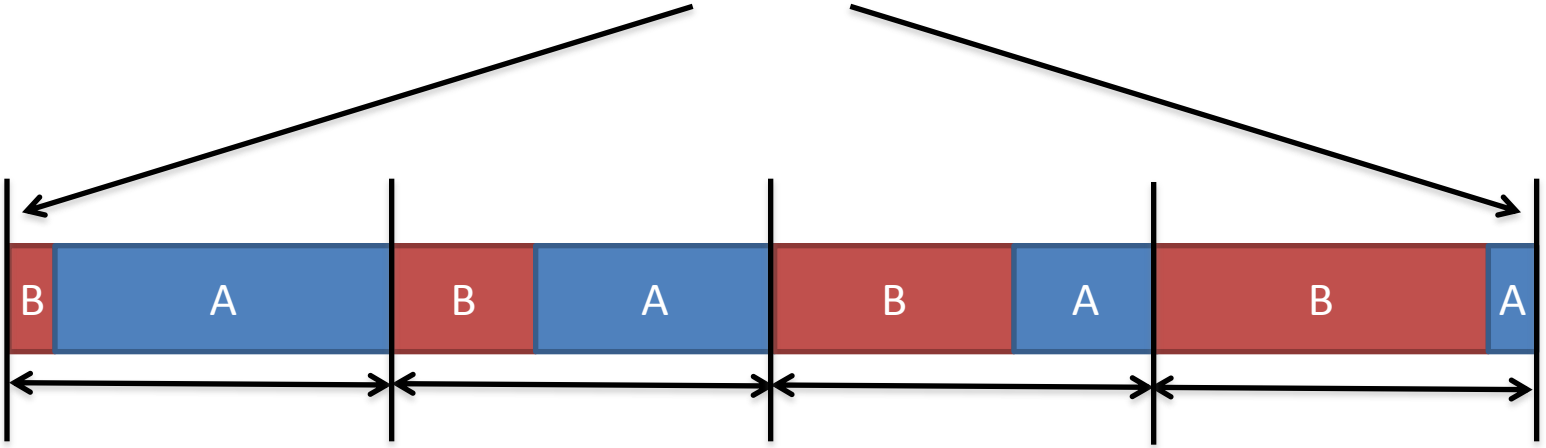


Tapered diblock composition profiles

Standard diblock:

Tapered “diblock”:





- Each division of two blocks (B then A) has the same length

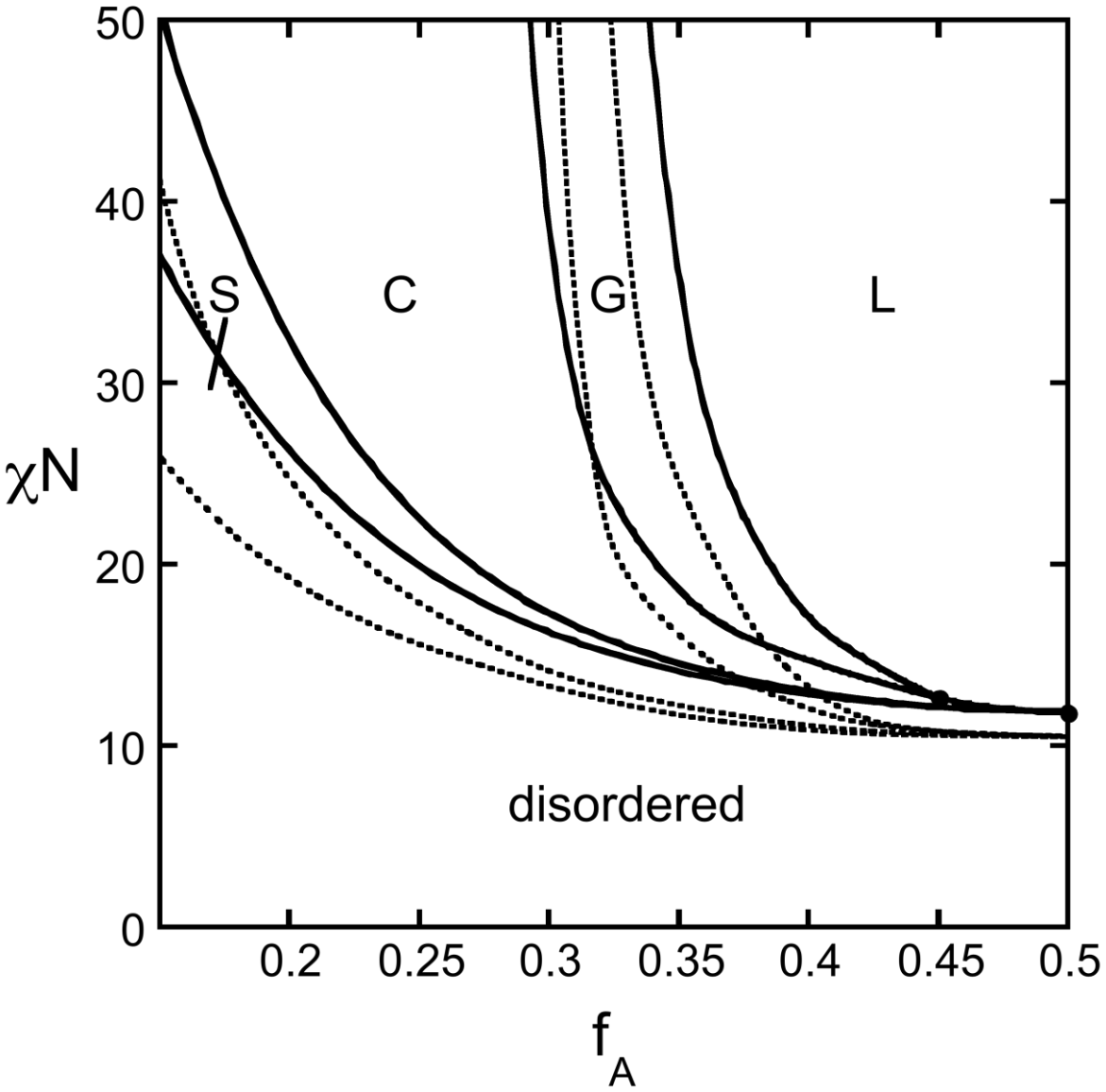
  (2% of polymer backbone)

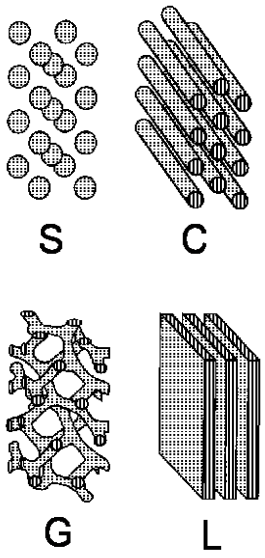
- Average composition matches the gradient

Jiang, R. *et al*. *Macromolecules* **41**, 5457–5465 (2008).

30% tapered phase diagram

dashed lines: diblock phase diagram

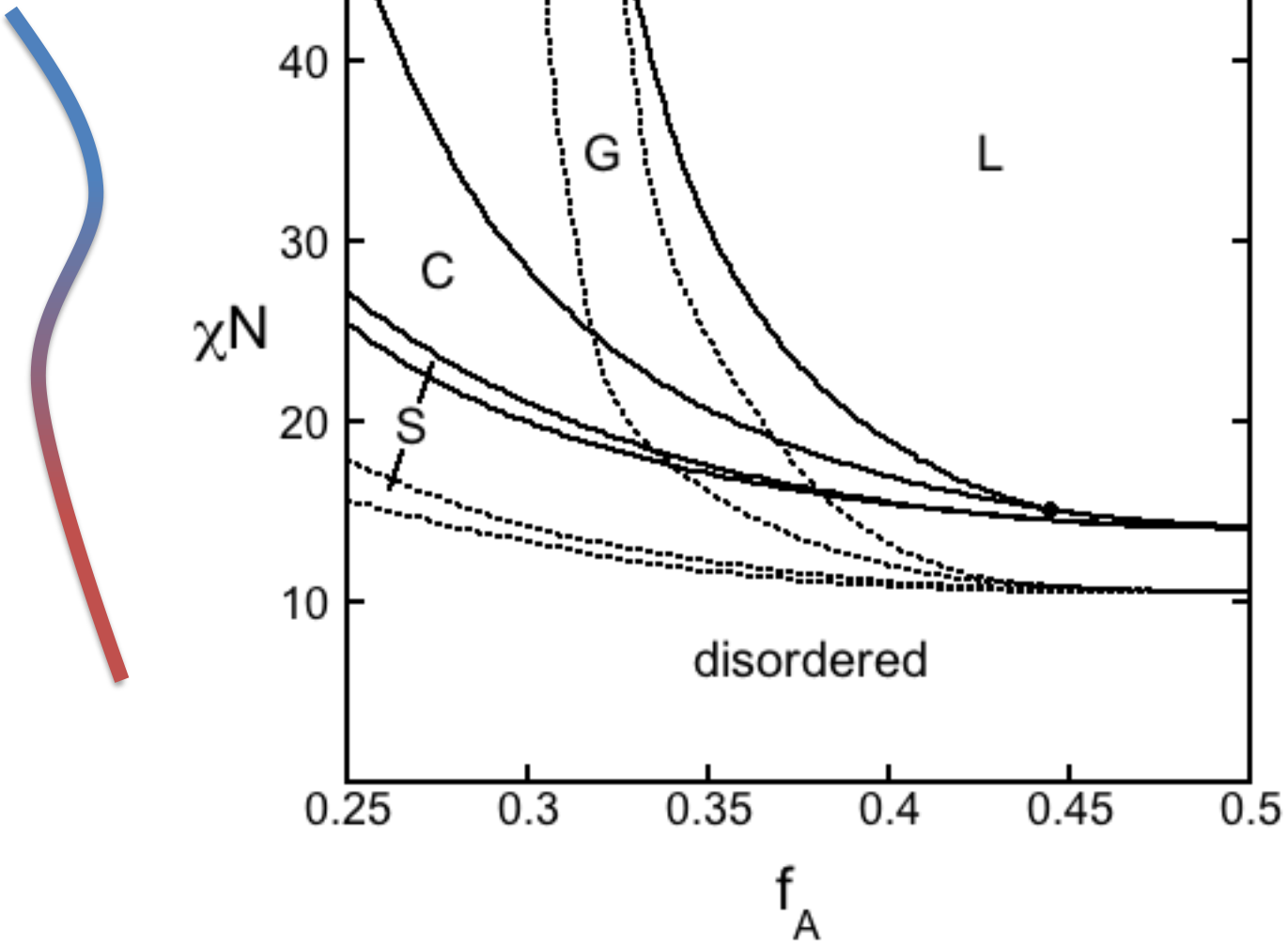


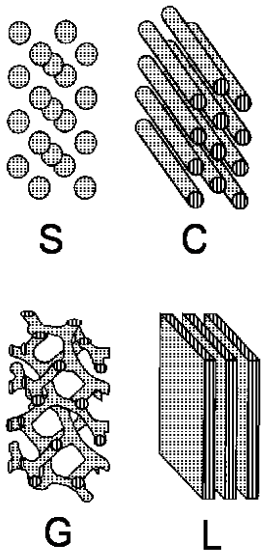


Dashed lines: diblock phase diagram adapted from Cochran, E. W., Garcia-Cervera, C. J. & Fredrickson, G. H. *Macromolecules* **39,** 2449–2451 (2006).

50% tapered phase diagram

dashed lines: diblock phase diagram

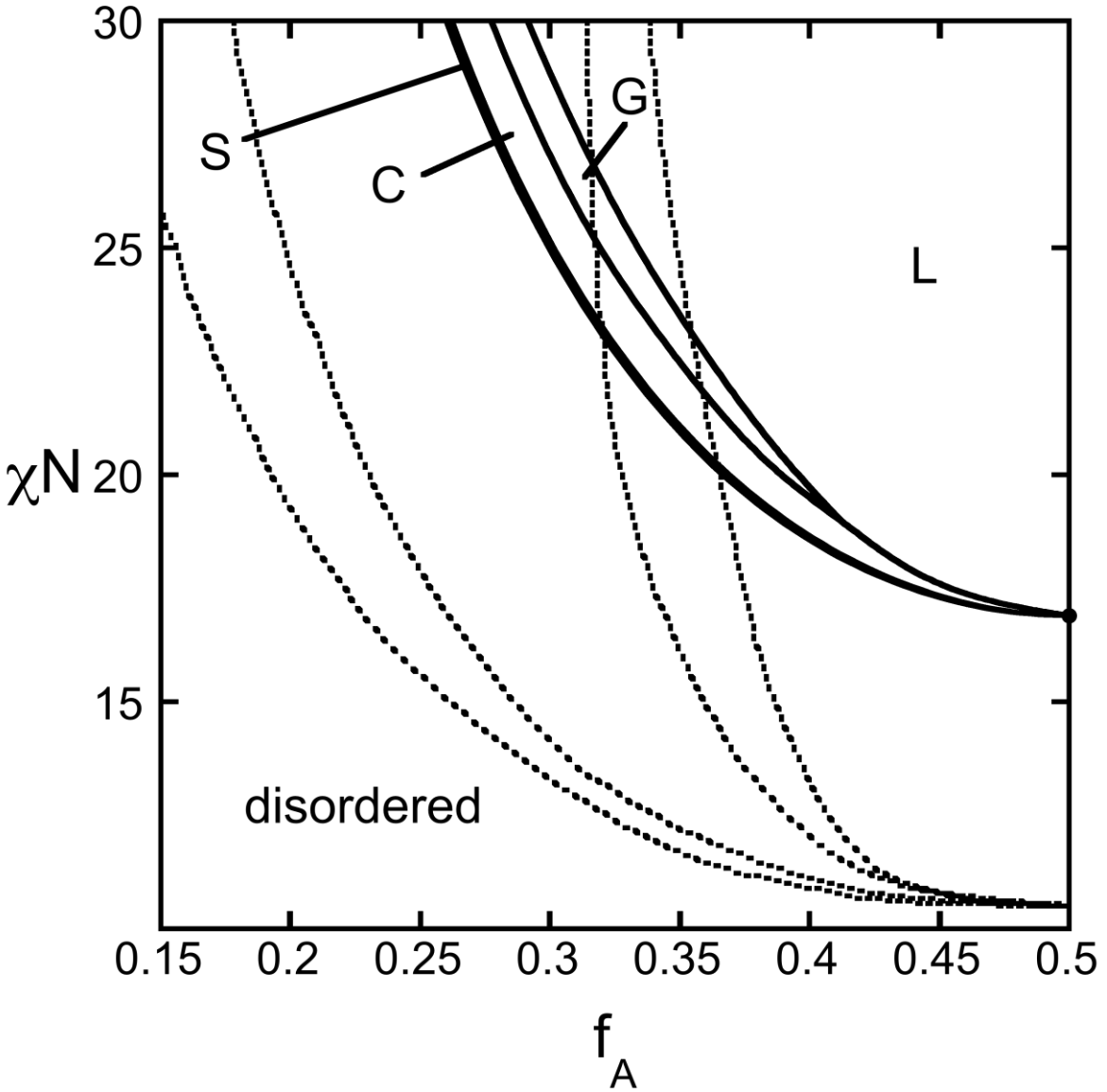


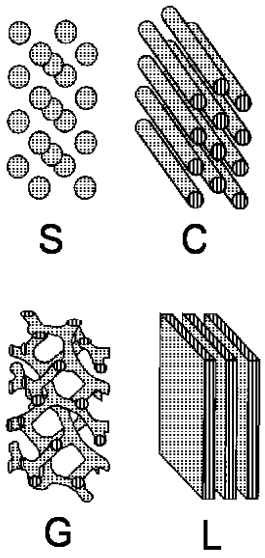


Dashed lines: diblock phase diagram adapted from Cochran, E. W., Garcia-Cervera, C. J. & Fredrickson, G. H. *Macromolecules* **39,** 2449–2451 (2006).

30% inverse tapered phase diagram

dashed lines: diblock phase diagram





Dashed lines: diblock phase diagram adapted from Cochran, E. W., Garcia-Cervera, C. J. & Fredrickson, G. H. *Macromolecules* **39,** 2449–2451 (2006).

Conclusions

- Taper shifts ordered phases to higher χN
- 30% taper: gyroid phase over a wider range of f_A
- 30% inverse taper: mostly lamellae
- Large inverse taper: snakes across/bridges lamellae
- Future work: replace SCFT with fluids DFT, add ions, and connect to MD simulations

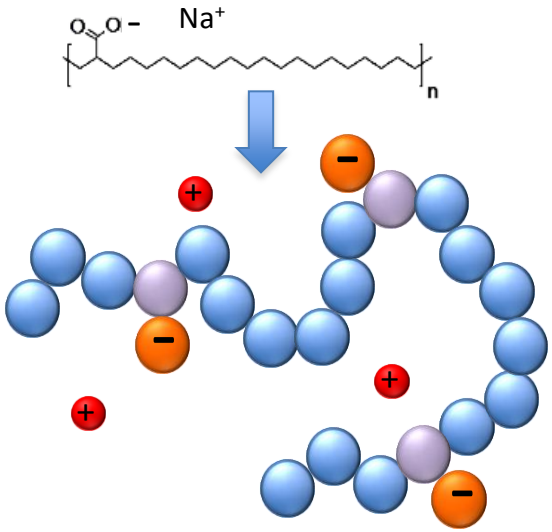
Acknowledgements

- Jonathan Brown
- Scott Sides
- OSU startup funding

Coarse-Grained MD Details

- Kremer-Grest bead-spring model (FENE bonds, repulsive LJ potential)
- NVT ensemble, Langevin thermostat, reduced LJ temperature = 1
- 35-36 backbone beads per chain (4-12 charges per chain)
  - 3 C-C bonds ~ one bead
  - Pendant (COO^-) same size as backbone bead (diameter = σ)
- Counterions half the diameter of polymer beads
- Equilibrate 10^7 steps of 0.005 τ (τ = reduced LJ time unit)
- 800 chains in simulation box, meltlike total packing fraction 0.366
- ε_r varies Coulomb interaction strength; **$\varepsilon_r = 4$** allows equilibration but still shows strong clustering, Bjerrum length = 36 σ ≈ 14 nm

Periodic



Random Block Copolymer