Recent Advances in Molecular Dynamics Simulations of Polymers

Mark J. Stevens

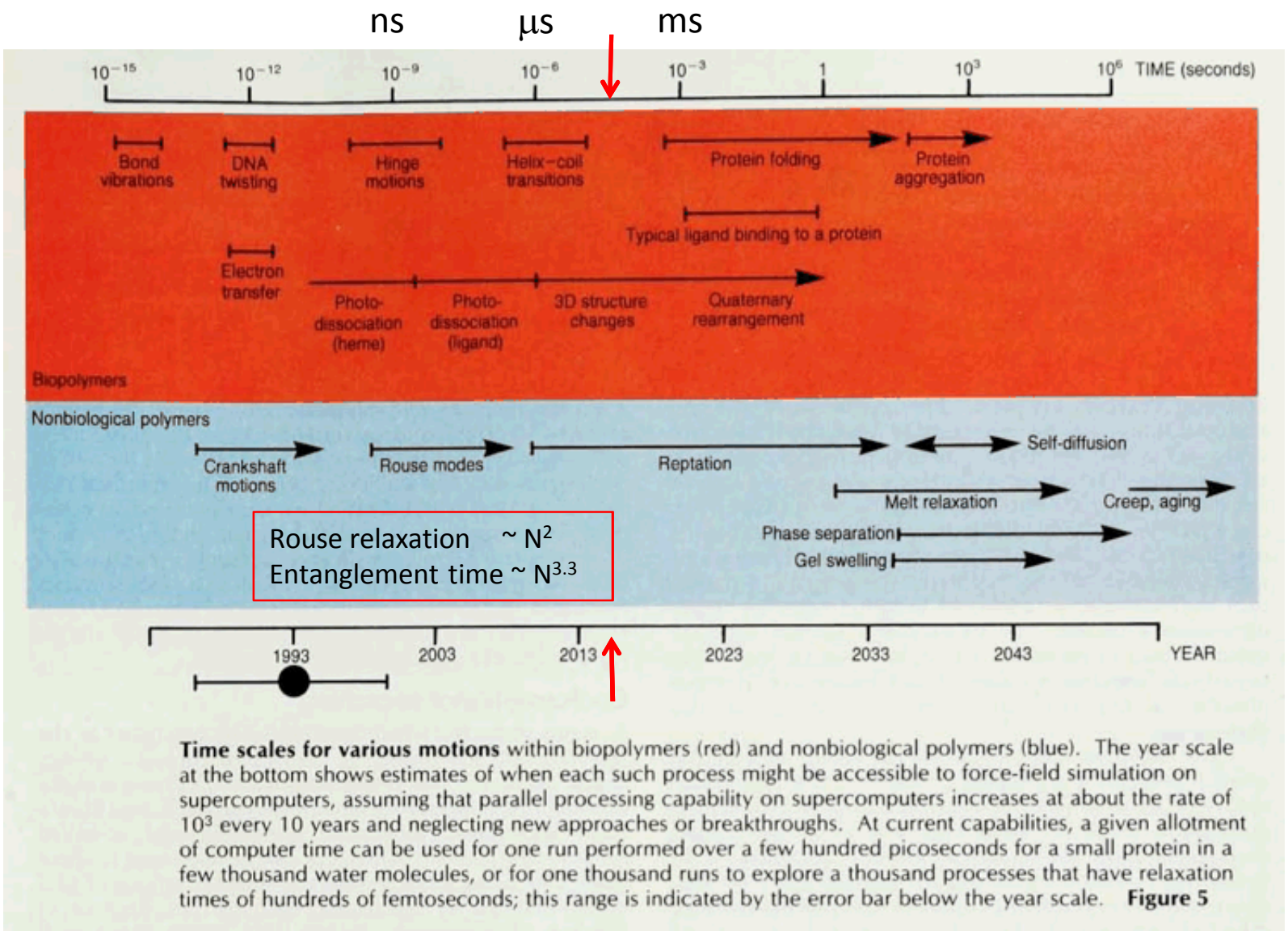
Sandia National Laboratories

Center for Integrated Nanotechnologies (CINT)
msteve@sandia.gov

U.S. DEPARTMENT OF ENERGY | Office of Science

Sandia is a multiprogram laboratory operated by Sandia Corporation, a Lockheed Martin Company, for the United States Department of Energy's National Nuclear Security Administration under contract DE-AC04-94AL85000.

Time Scales in Polymers



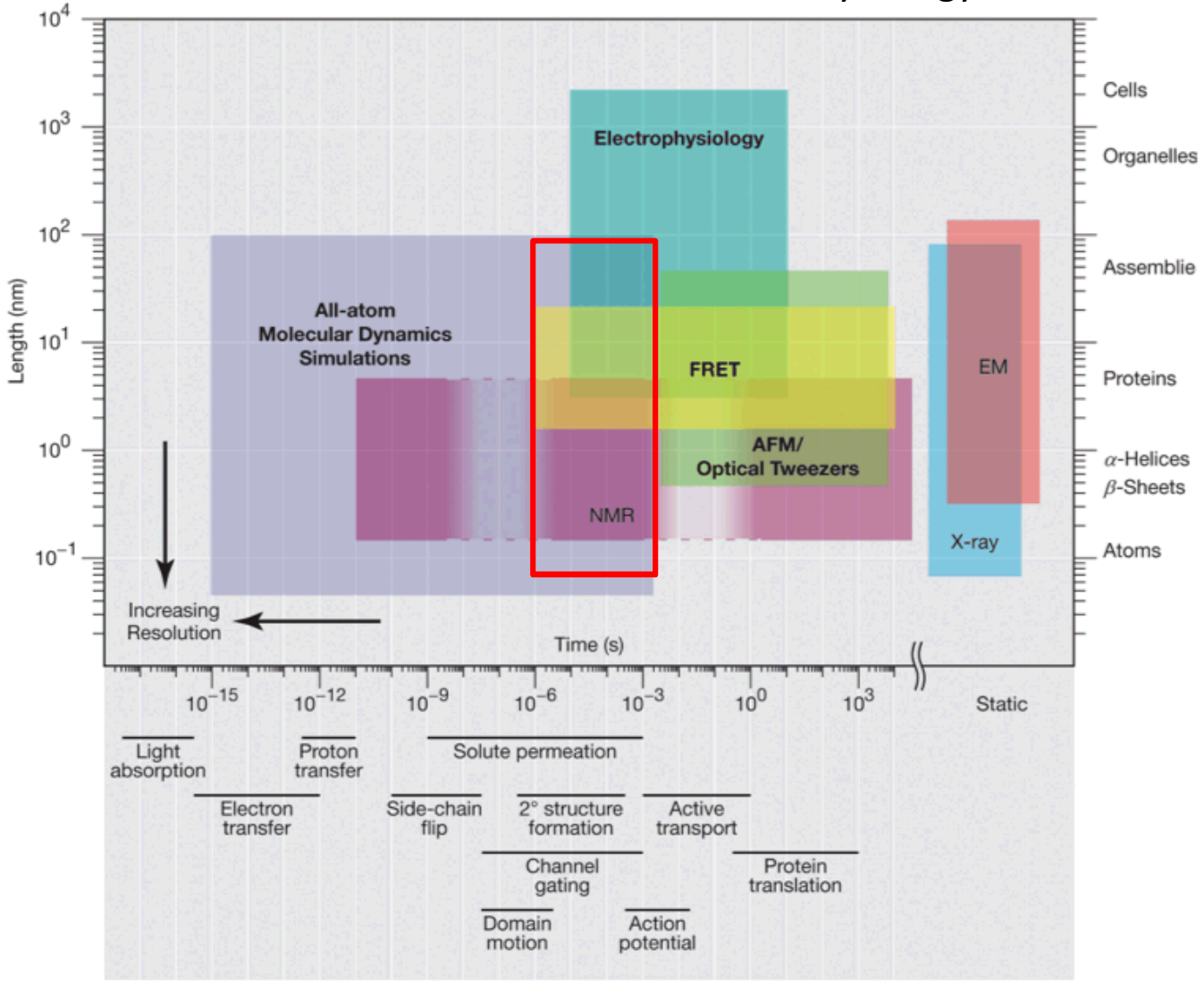
Time scales for various motions within biopolymers (red) and nonbiological polymers (blue). The year scale at the bottom shows estimates of when each such process might be accessible to force-field simulation on supercomputers, assuming that parallel processing capability on supercomputers increases at about the rate of 10^3 every 10 years and neglecting new approaches or breakthroughs. At current capabilities, a given allotment of computer time can be used for one run performed over a few hundred picoseconds for a small protein in a few thousand water molecules, or for one thousand runs to explore a thousand processes that have relaxation times of hundreds of femtoseconds; this range is indicated by the error bar below the year scale. **Figure 5**

Hue Sun Chan and Ken Dill, Physics Today (1993)

Mark Stevens
msteve@sandia.gov

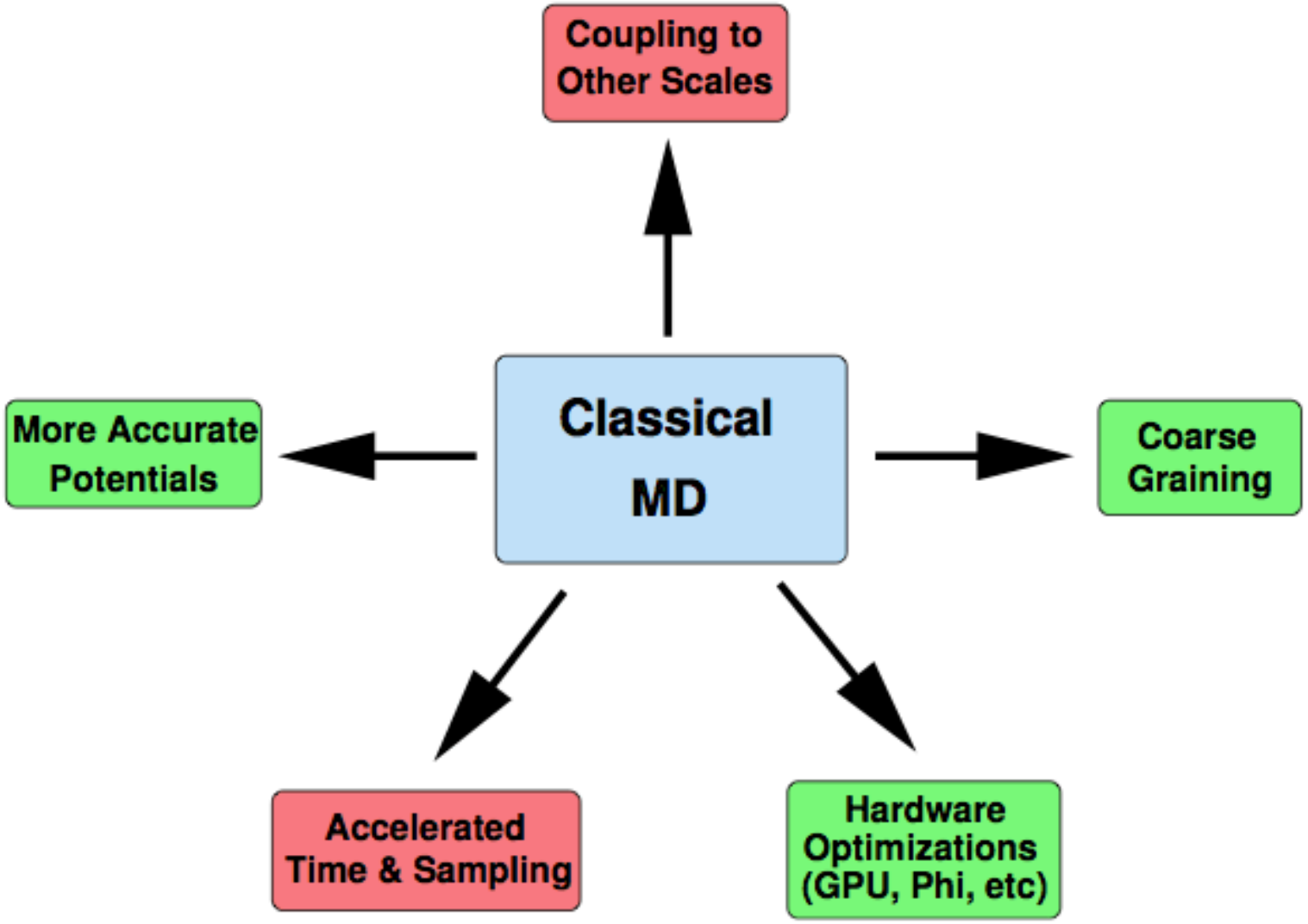
Scales (biological)

Dror, Jensen, Borhani & Shaw, J. General Physiology 2012



Mark Stevens
msteve@sandia.gov

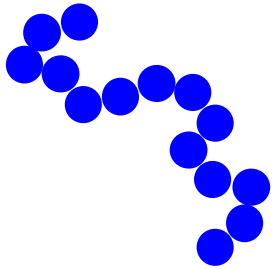
Research Directions in (Polymer) MD



Mark Stevens
msteve@sandia.gov

Modeling Epoxies

Limited in time and length scales

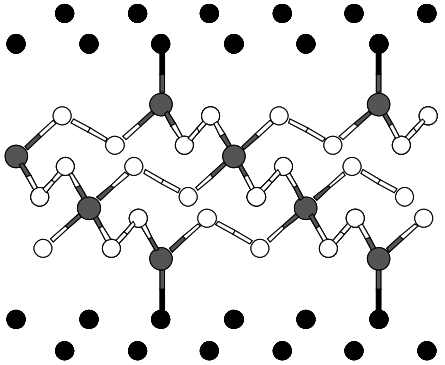


- Polymer models (in general)
  - coarse-grained models to treat long time scales
    - bead spring model
    - random walk paradigm
    - focus is on trends (not single quantities) & molecular mechanisms
  - atomistic models
    - available time scales typically too short
      - time step = 1 fs $\Longrightarrow$ total time ~ 10-100 ns
    - more appropriate for the liquid mixture interaction with surface
    - force-fields available need to be improved
- Epoxies
  - complex chemical structure $\Rightarrow$ atomistic simulations unreasonable
  - glass $\Rightarrow$ weak strain rate dependence
  - **view as highly crosslinked polymer network**

Mark Stevens
msteve@sandia.gov

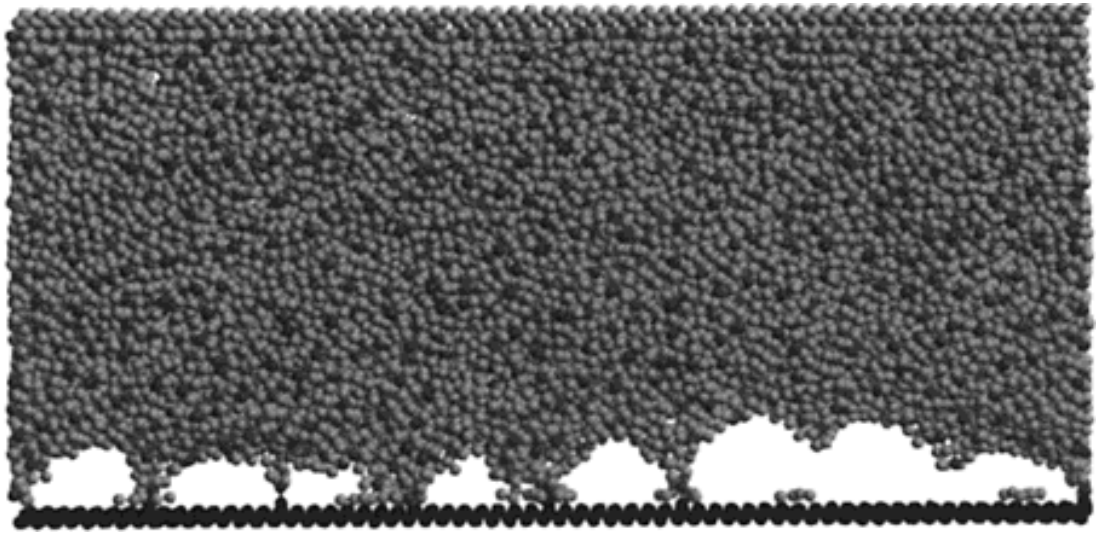
Model Epoxy Simulations

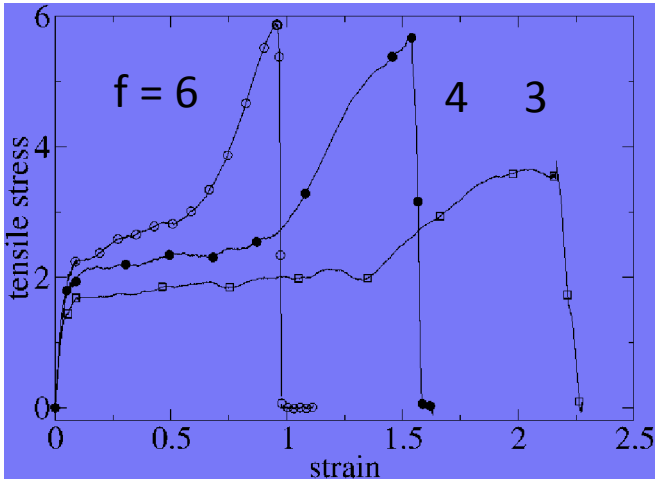
About a decade ago we started modeling epoxies as a highly crosslinked polymer network.



Examined many aspects of the adhesion and fracture.

- effect of number of bonds at surface
- functionality of the crosslinker
- found very large failure strains



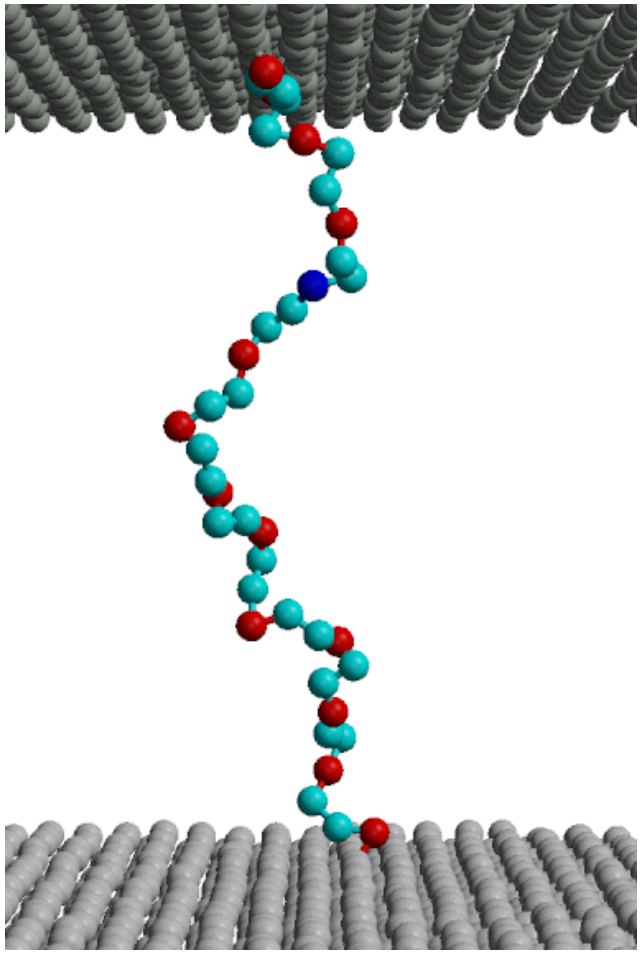


Mark Stevens
msteve@sandia.gov

Failure Strain: Minimal Paths in Network

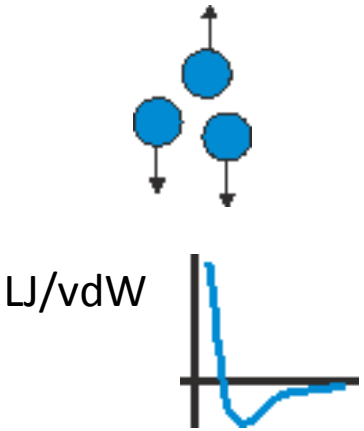
For each bond to the top surface there is a **minimal path** of length *P* through the network to the bottom surface

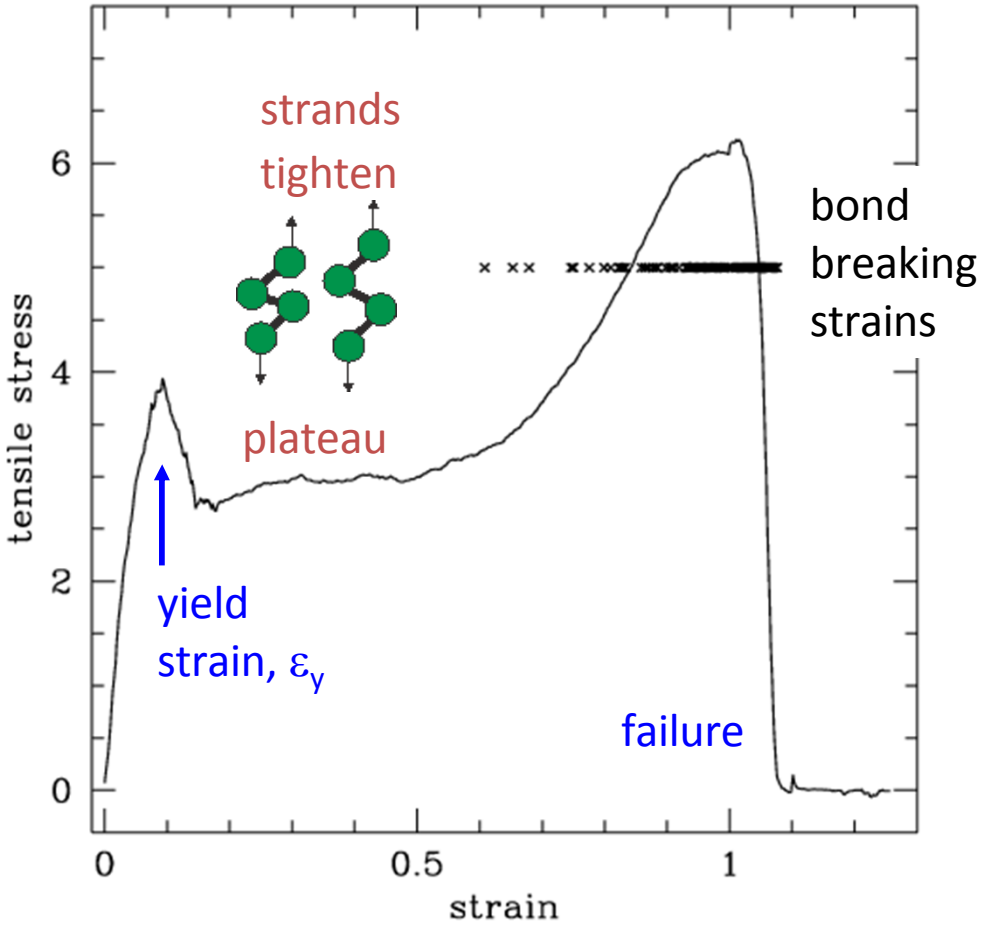
- Failure strain is determined by maximum minimal path
  - At the strain equivalent to the maximum *P,* all bonds in the paths connecting the two surfaces must be stressed
- In the presence of defects, failure occurs at smaller strains, because of nonuniform strains.



Mark Stevens
msteve@sandia.gov

Tensile stress-strain curve: Molecular Mechanisms

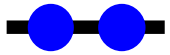




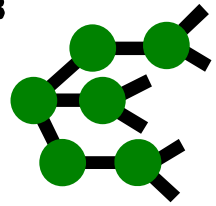
Mark Stevens
msteve@sandia.gov

Model Epoxy

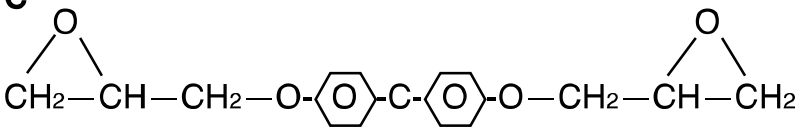
A



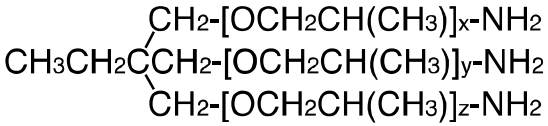
B



C



D



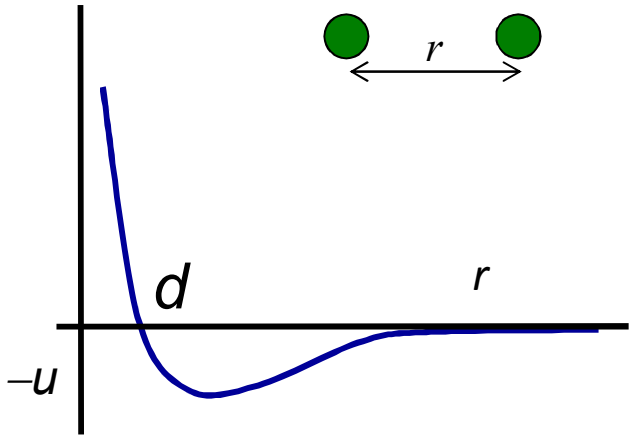
x+y+z = 5

Mark Stevens
msteve@sandia.gov

Potentials

Lennard-Jones (LJ) potential (van der Waals)

$$4u\left[\left(\frac{d}{r_{ij}}\right)^{12}-\left(\frac{d}{r_{ij}}\right)^{6}\right]$$

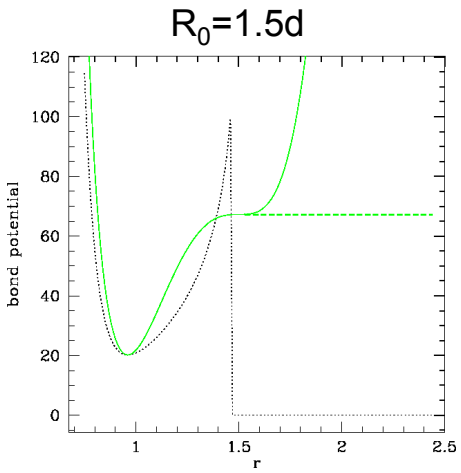


- Energy unit: u
- Length unit: d
- Here all types equivalent

Bond potential

- FENE (non breakable) = $-kR_0 \log(1-(r/R_0)^2)$
- breakable (smooth quartic)

No angle potential: full flexible chains

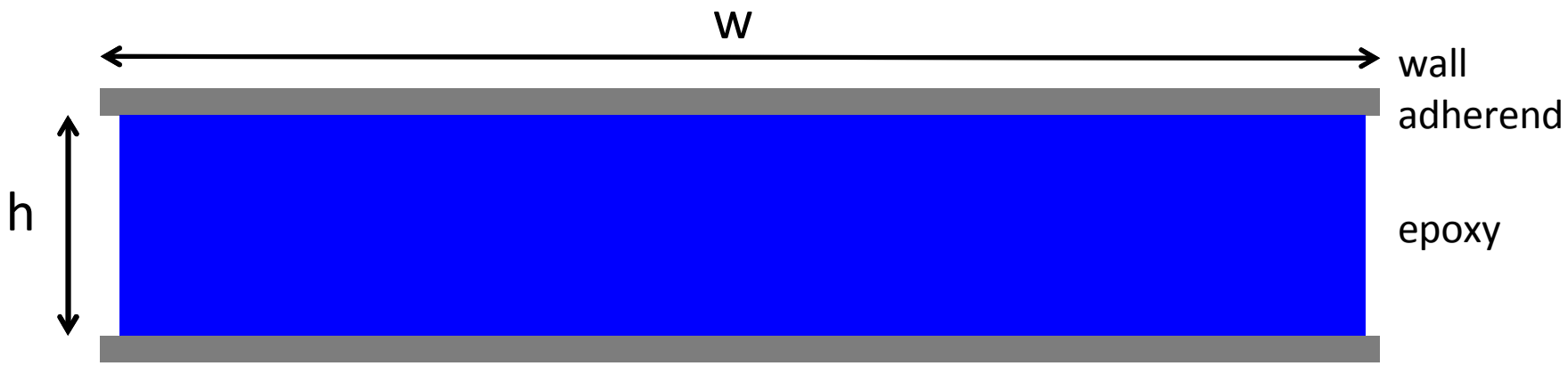


Mark Stevens
msteve@sandia.gov

Systems

TABLE I. Systems

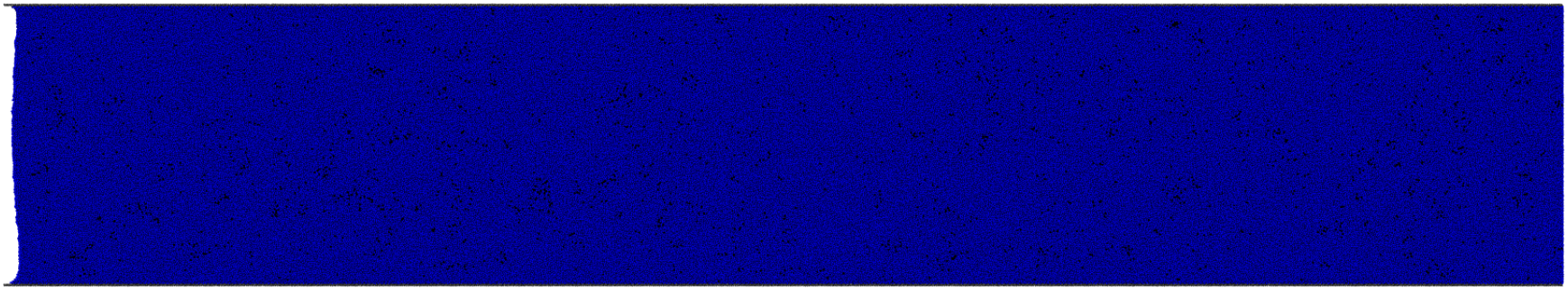
index	N	h (d)	w (d)
1	513600	40.4	417.1
2	1975200	76.1	834.2
3	7747200	149.0	1668.3
4	17316000	222.3	2502.5
5	30681600	295.0	3366.6



Mark Stevens
msteve@sandia.gov

Tensile pull

$\varepsilon = 0.00$

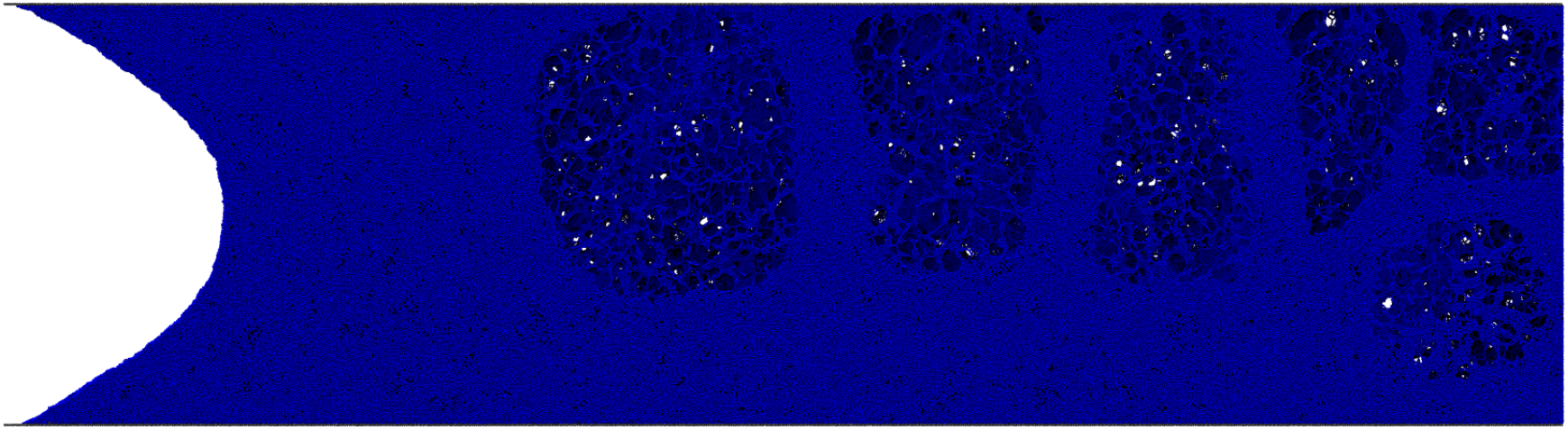


Only left half of system is shown

Mark Stevens
msteve@sandia.gov

Tensile pull

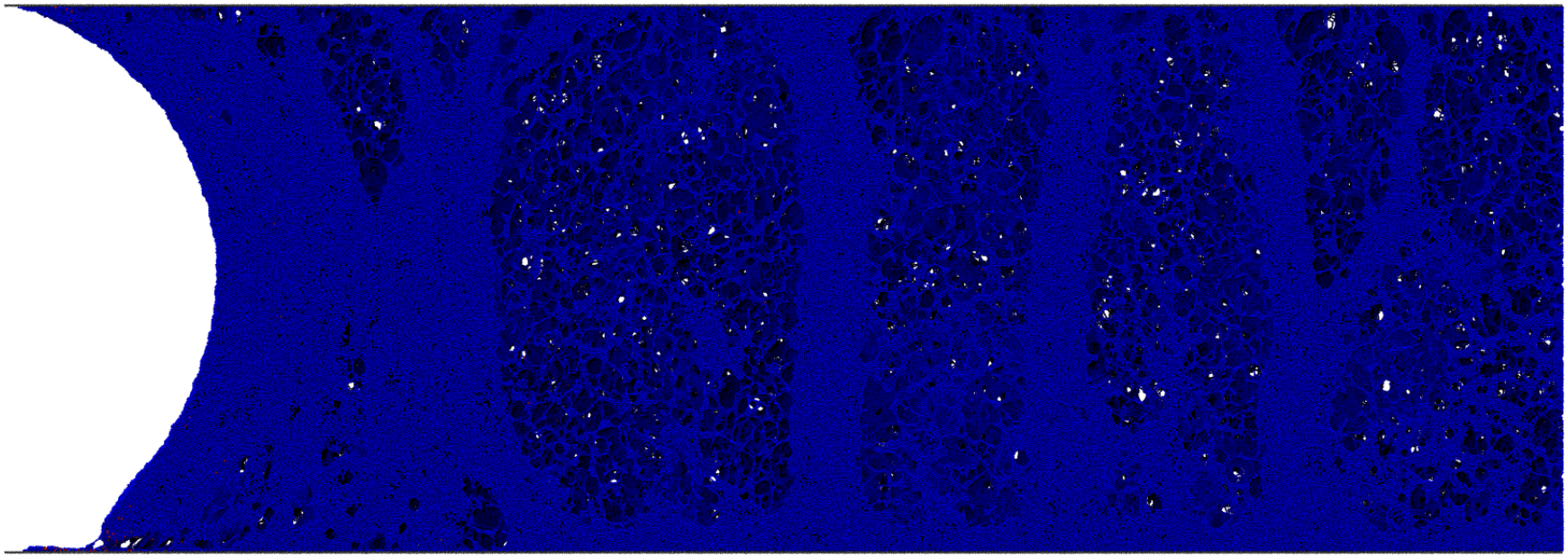
$\varepsilon = 0.50$



Mark Stevens
msteve@sandia.gov

Tensile pull

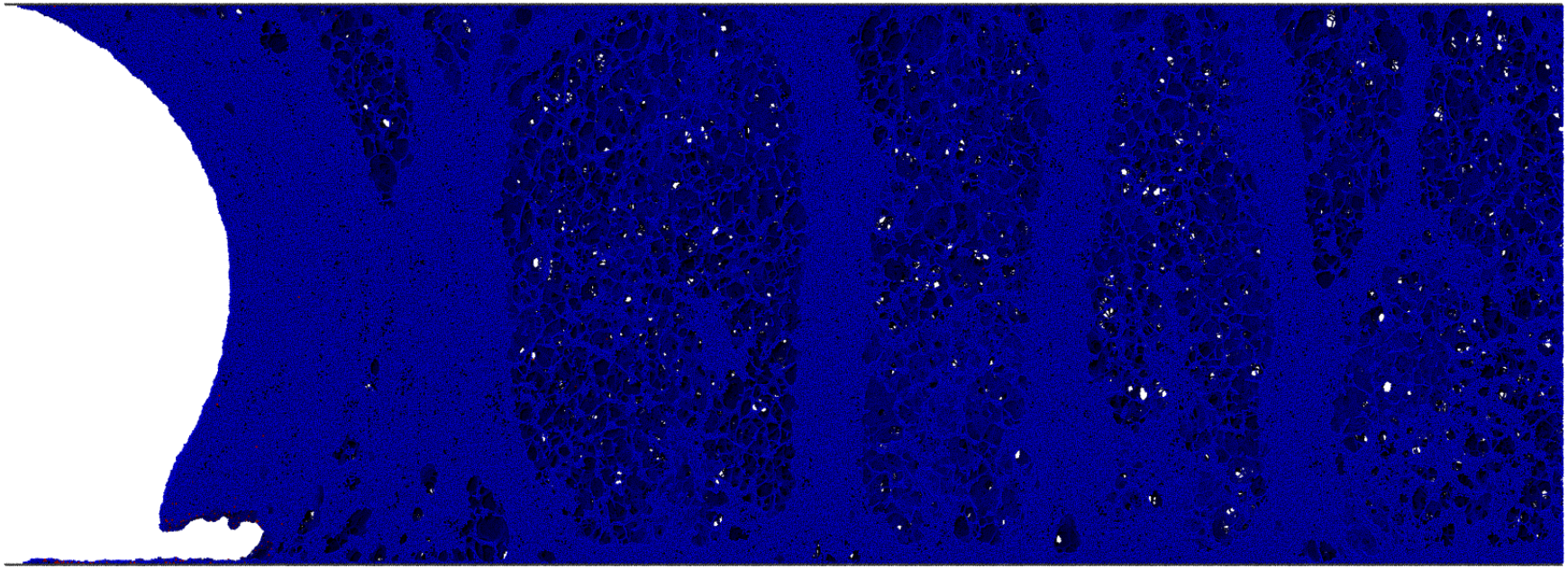
$\varepsilon = 0.95$



Mark Stevens
msteve@sandia.gov

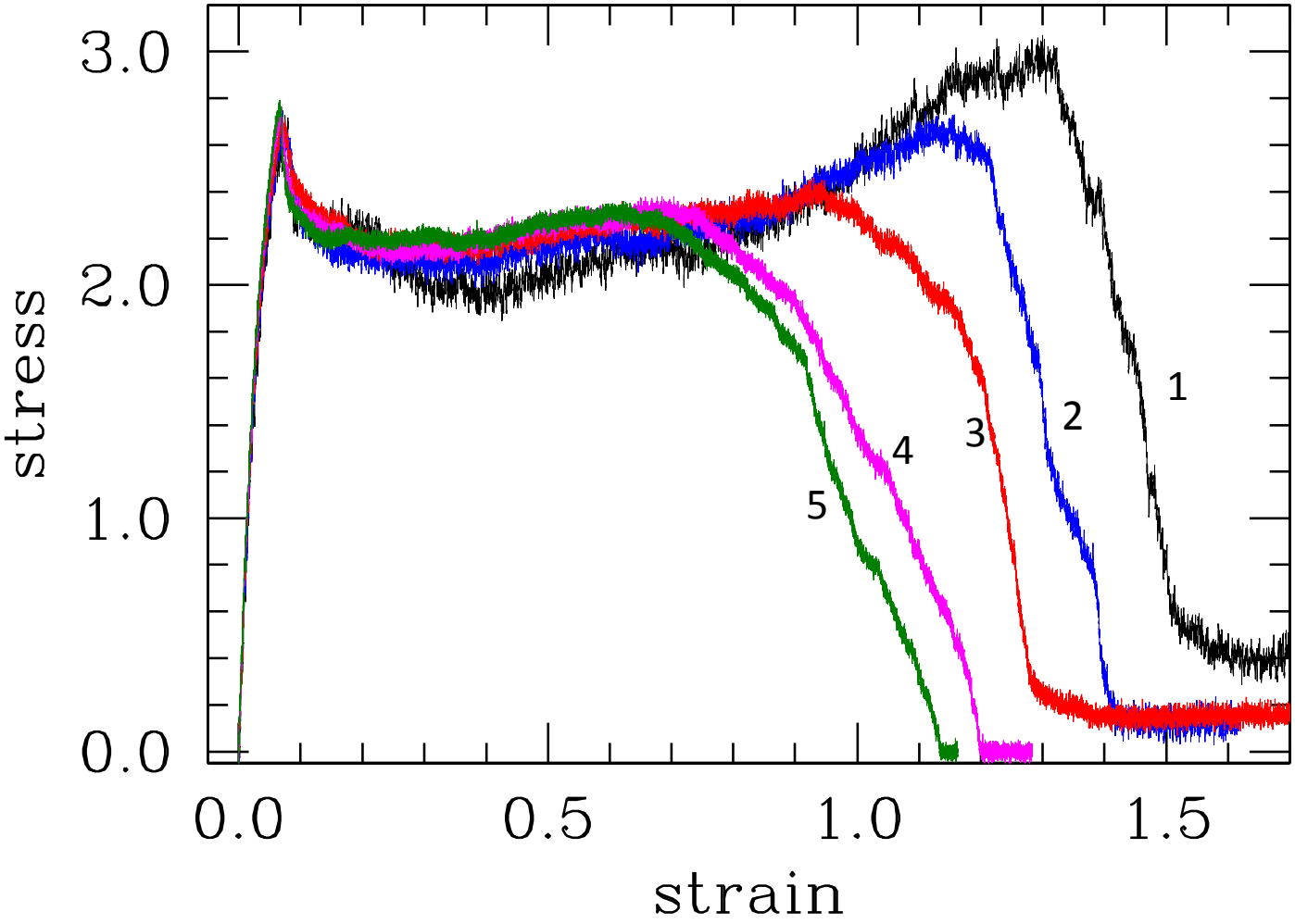
Tensile pull

$\varepsilon = 1.00$



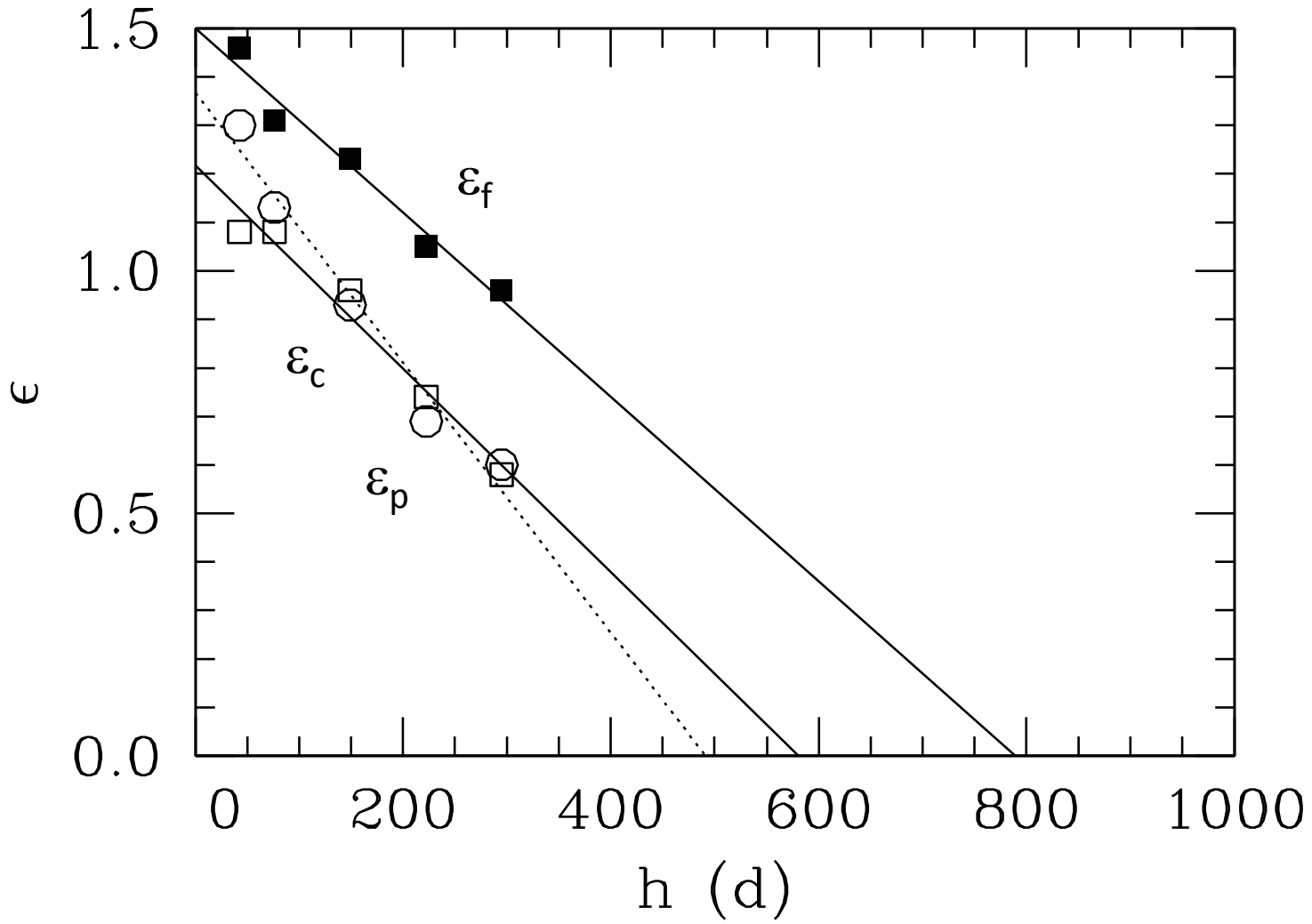
Mark Stevens
msteve@sandia.gov

Stress-strain curves



Mark Stevens
msteve@sandia.gov

System Size Dependence



Mark Stevens
msteve@sandia.gov

Conclusions

Crack initiation at corners does occur within molecular simulation.

Failure strain is strongly system size dependent in these ‘small’ systems.

Stress is noticably concentrated at corners for small strain.

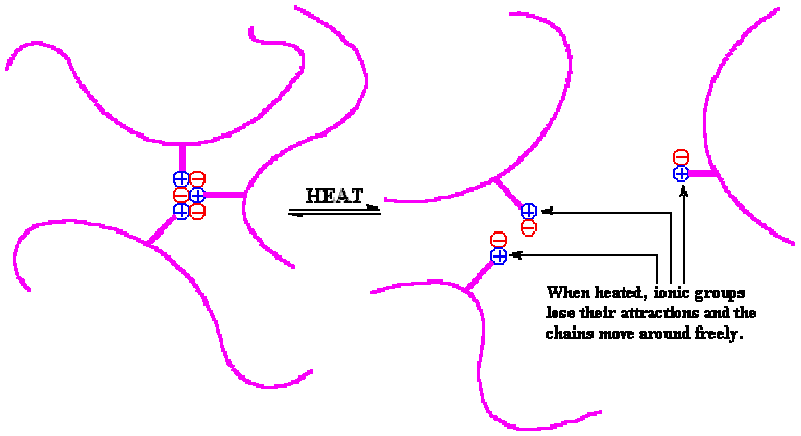
Shear stress in corner important because of lateral contraction at sides yields an acute angle of the polymer network surface in the corner.

Mark Stevens
msteve@sandia.gov

Ionomers

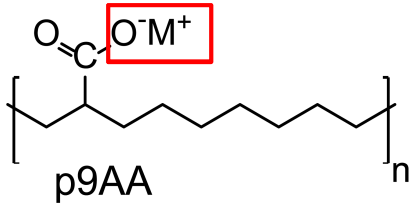
Ionomers are polymers that contain a small fraction of ions.
No solvent (melt). Focus here is on dry ionomers.

ε ~ 2-10 ⇒ **strong electrostatic** interactions (~ 40 kT)



Conductivity low

- needed for Li-ion batteries: ≥ 10^{-3} S/cm
- ionomers: generally < 10^{-5} S/cm
- ionic aggregates



Ken Wagener synthesis (ADMET) of precisely spaced charges

Acrylic acid Neutralization level*

p9AA–43%Li

Precise spacer length (p9, p15, p21)

Counterion type
Li^+, Na^+, Cs^+, Zn^{2+}

Compare to experiment by Karen Winey's group

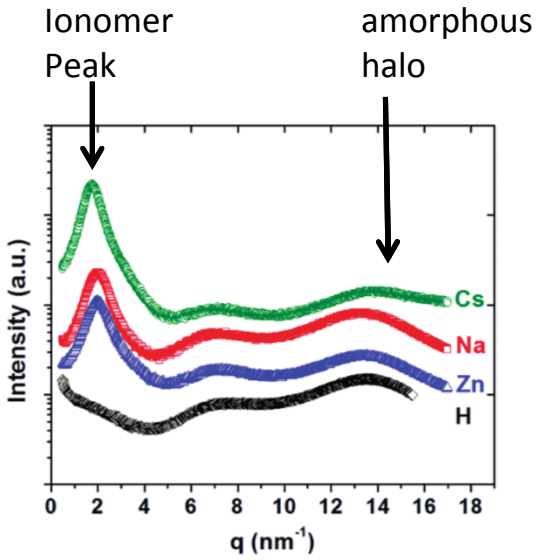
Mark Stevens
msteve@sandia.gov

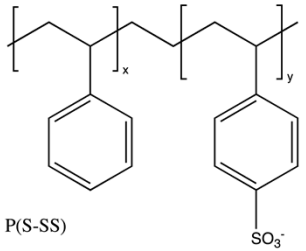
Aggregates & Ionomer Peak

How do we know there are aggregates?

- low wavevector peak in scattering
- from inter-aggregate scattering
- ubiquitous

$q \sim 2/\text{nm} \Longrightarrow d \sim 3\ \text{nm}$

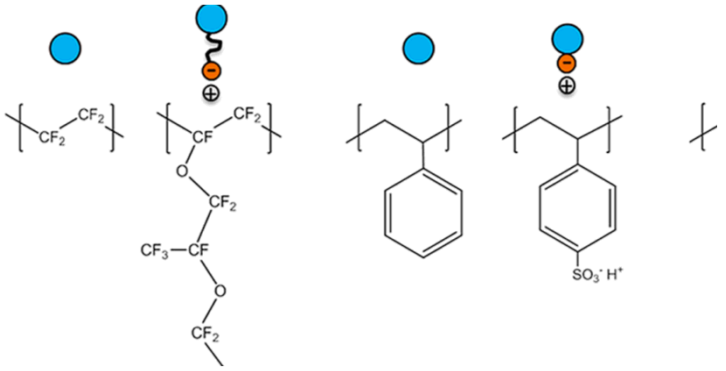




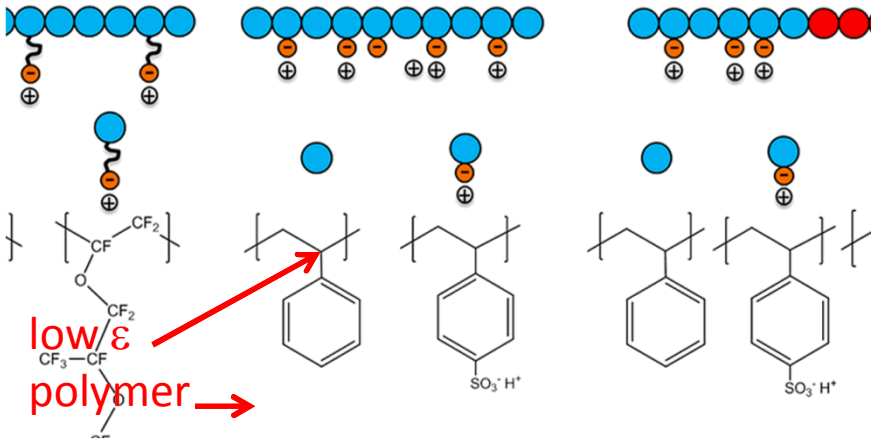
A. M. Castagna, et al. *Macromolecules*, **2011**

Old Picture

Beers & Balsara. 2012



Spherical aggregates of ions that form a liquid ordered structure.



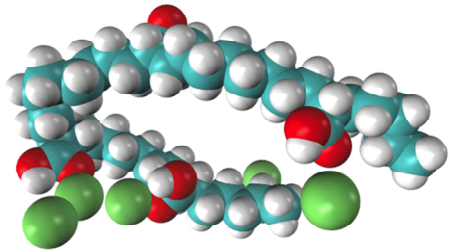
Dynamics: Ions hop from one cluster ***across low dielectric*** to another.

Mark Stevens
msteve@sandia.gov

Ionomer Simulations

Atomistic model

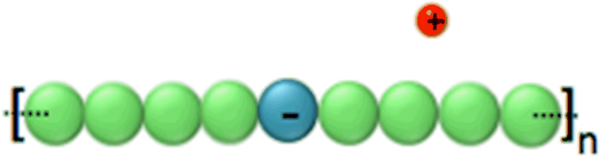
- treat different counterions
- treat neutralization
- compare directly to experiment
- atomistic detail
- dynamics limited



Coarse-grained bead spring model

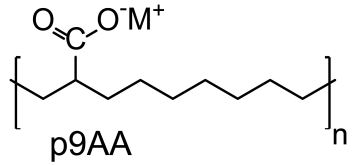
- simpler physics:

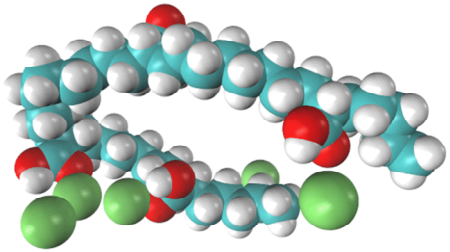
  focus on ionic interactions with polymeric constraints
- get to Fickian diffusion regime
- also with Electric field



Mark Stevens
msteve@sandia.gov

Atomistic Ionomer Simulations





- Variations in:
  - **cation** type: M^+ = Li^+, Na^+, Cs^+, Zn^{2+}
  - **neutralization** level = % COO^-M^+ vs COOH
  - **spacing** between acid groups (***n*** = 9, 15, 21)

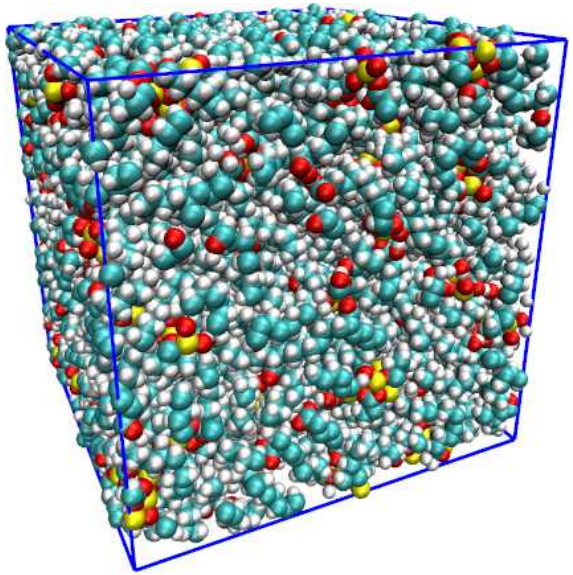
For comparison with Winey group data

- All atom OPLS force-field
- 4 monomers per chain (4 acid groups)
- 200 chains for p9
- ~ 64 Å box, total of ~25,000 atoms
- **T = 150 C** (above T_g)
- **30 ns** (**400 ns** in one case)
- replica & multiple starting states simulations to check

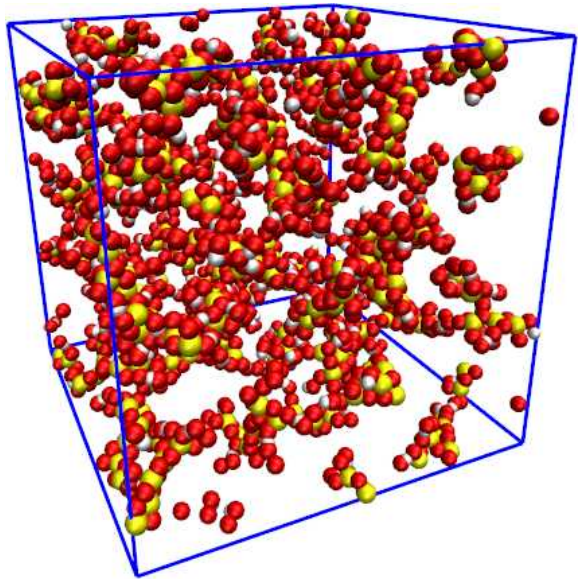
Mark Stevens
msteve@sandia.gov

MD Simulations

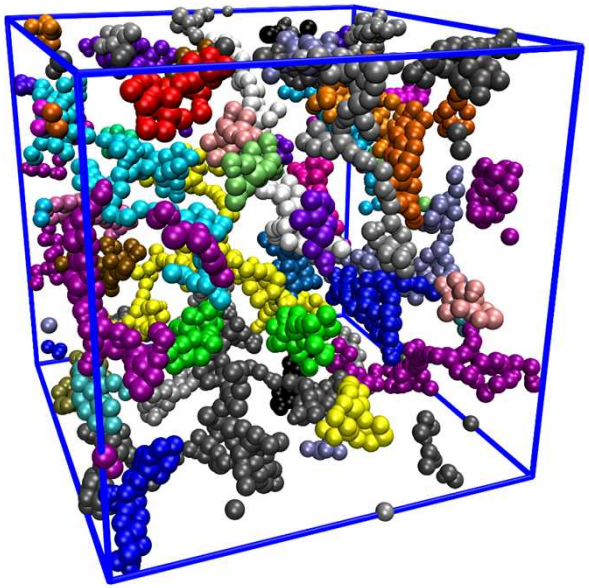
p9AA-43%Li



All atom simulations



Ionic aggregates (Li & O only)



Cluster analysis

Radial distribution functions
- cluster definitions

S(q)
- see ionomer peak
- compare to experiment

Cluster analysis
- structure of aggregates ….

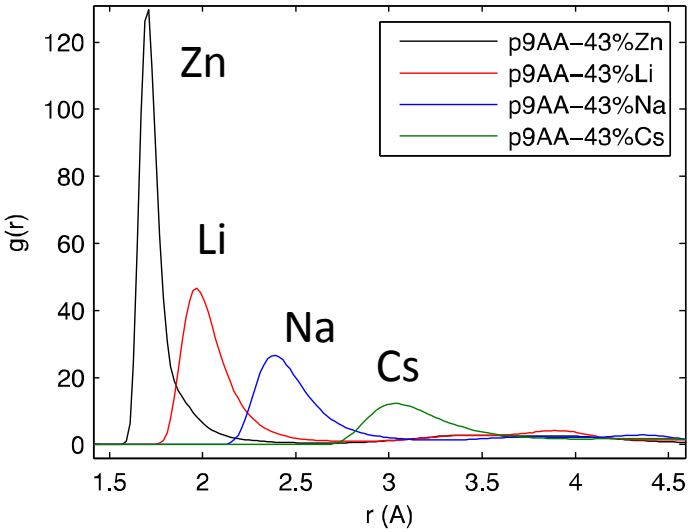
Mark Stevens
msteve@sandia.gov

Correlation functions: local ionic aggregation

O^{-}-M^{+} **– +**

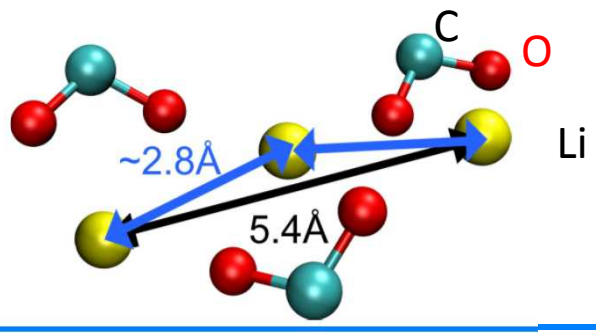
- very large peaks
- peak position ~ ion size
- height decreases for larger ions

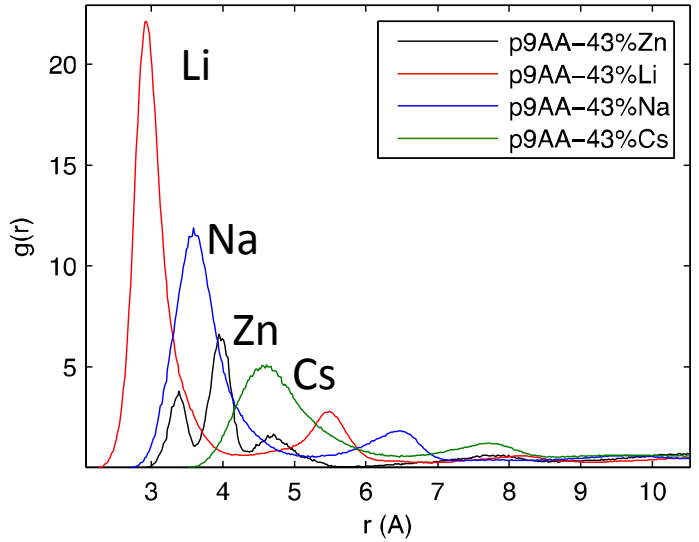
cluster analysis:
O-ion in same cluster if separation within 1st peak
carbonyl O (OH) in same cluster



M^{+}-M^{+}

- 1st peak at next-nearest neighbor distance
- secondary peaks visible (aggregate size)
- Zn^{++} is an exception



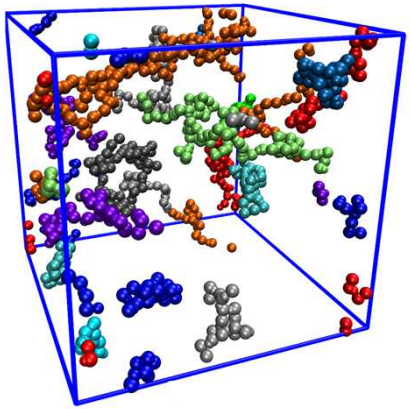


Mark Stevens
msteve@sandia.gov

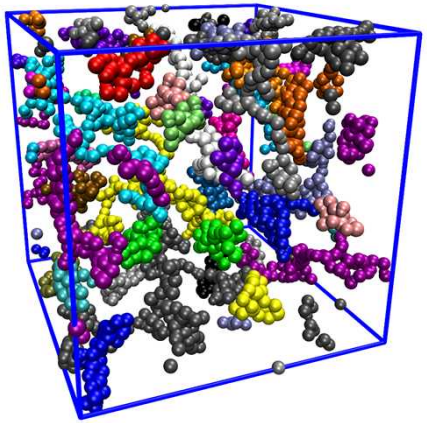
Morphology: Effect of Neutralization

Coloring by cluster: only show O & Li

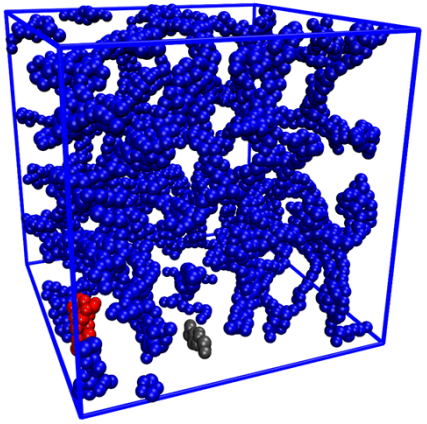
p9AA-**N**%Li



10%

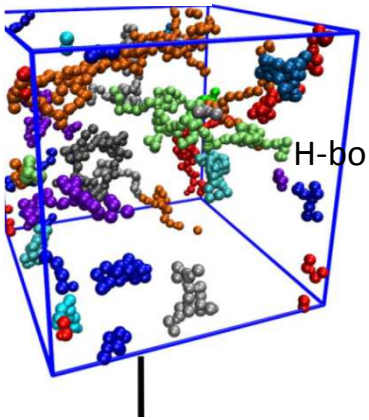


43%

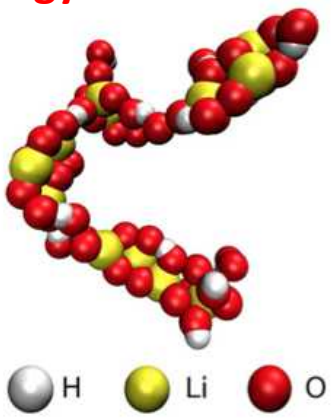


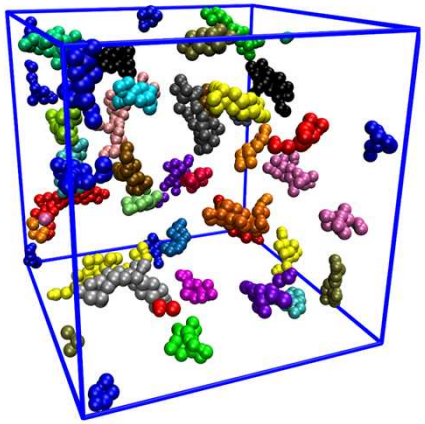
100%

Clusters are stringy



H-bonds important





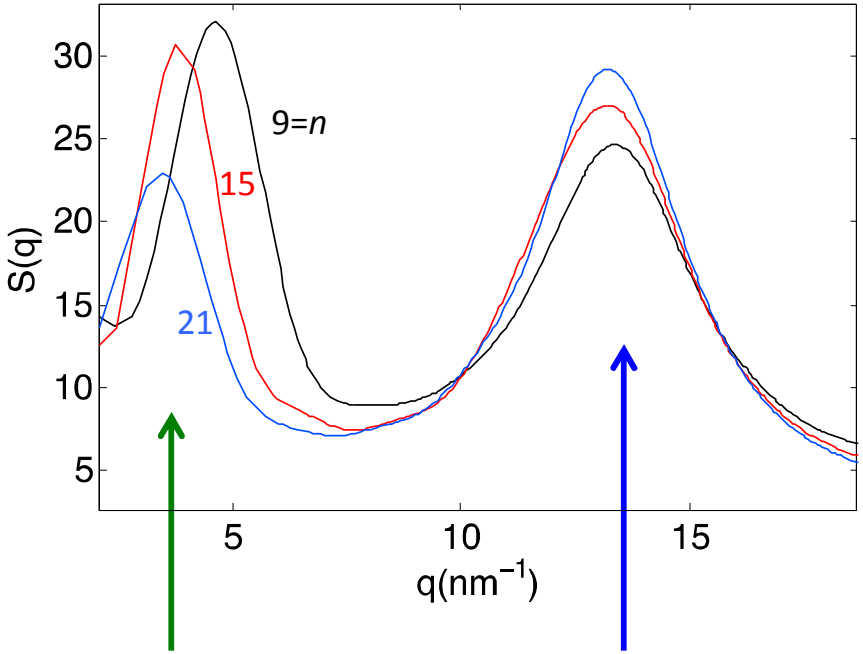
p21AA-43%Li

Mark Stevens
msteve@sandia.gov

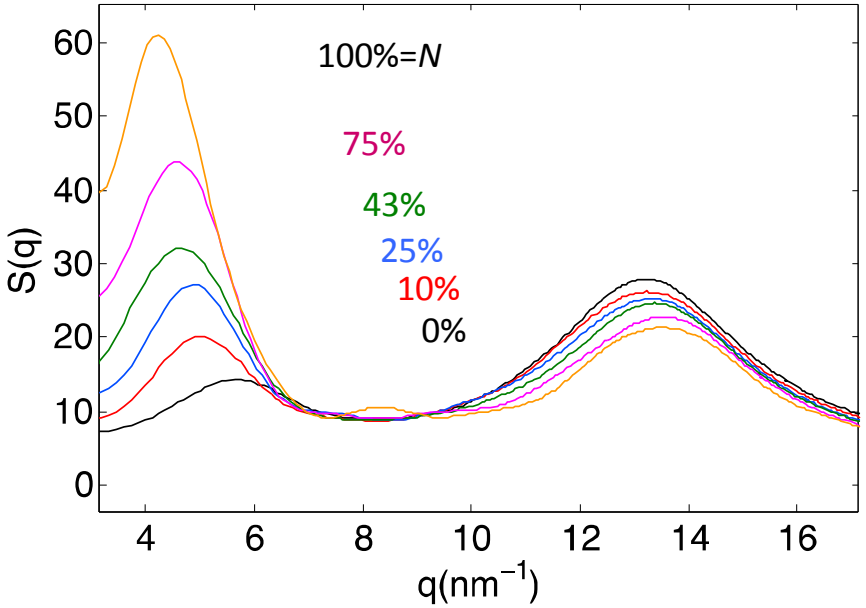
Total Structure Factors for Li-neutralized pAA

$$S(q) = \sum_i c_i f_i^2 + 4\pi\rho \int_0^\infty \frac{\sin(qr)}{qr} r^2 \sum_{i,j} c_i c_j f_i f_j \big(g_{ij}(r) - 1\big) dr$$

vary spacer: p*n*AA43% Li



vary neutralization: p9AA*N*% Li



Ionomer Peak Amorphous Peak

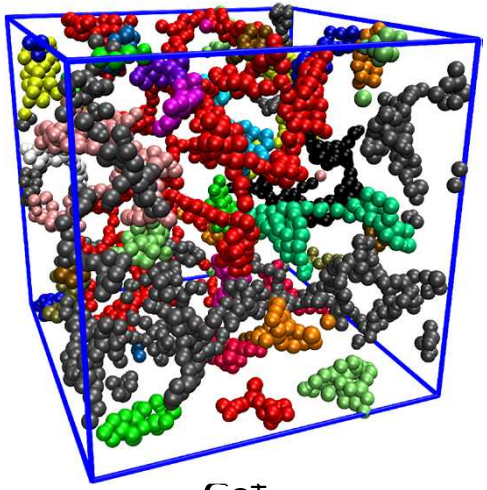
Spacing of aggregates changes with neutralization and spacer length.

Mark Stevens
msteve@sandia.gov

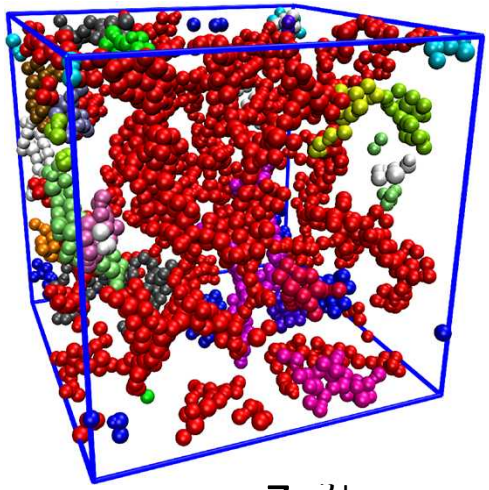
Morphology for Different Cations

p9AA-43%**M**

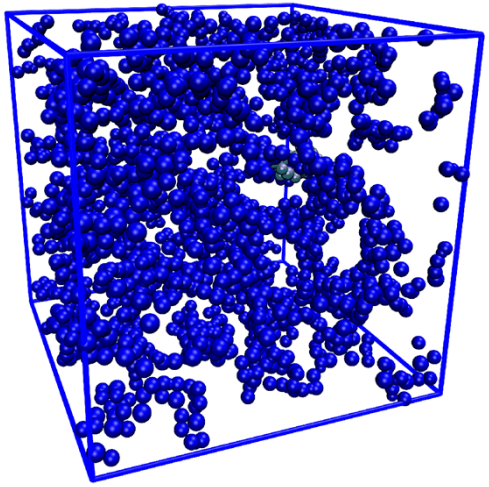
Li^+



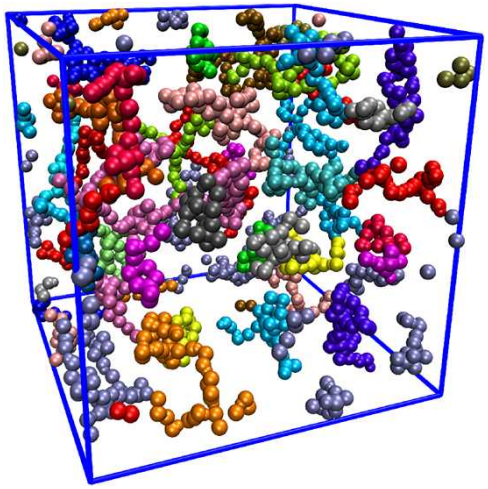
Na^+



Cs^+



Zn^{2+}



Color by distinct aggregate

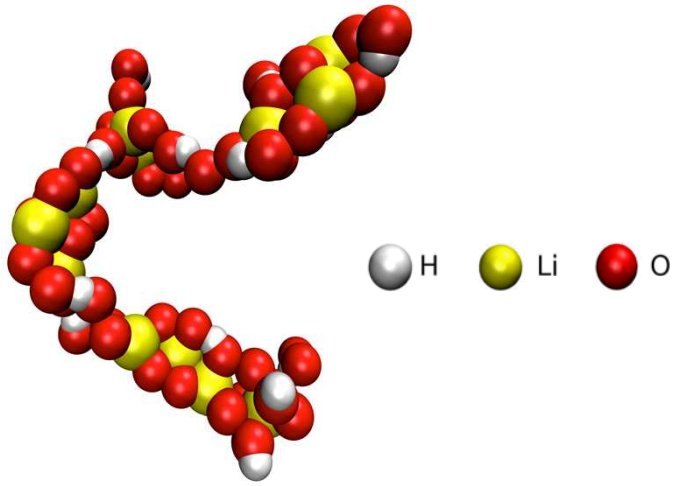
- Broad variety of morphologies
- Very different from spherical/ liquid-like order previously assumed
- Geometry not discernable from S(q)

Mark Stevens
msteve@sandia.gov

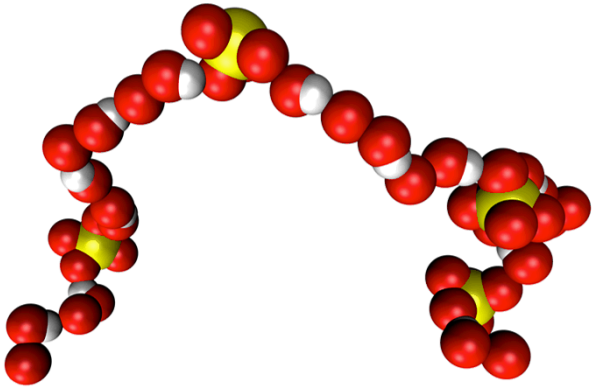
Stringy Aggregates

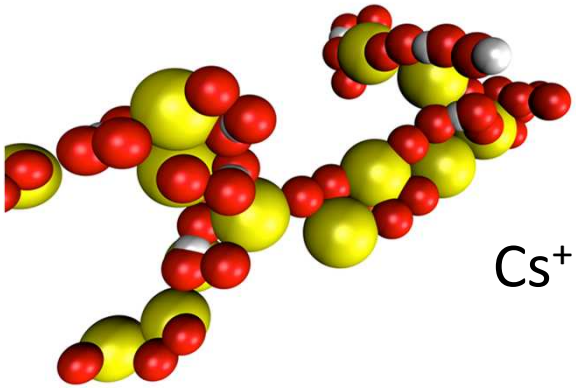
p9AA-43%

Li^+



Zn^{2+}

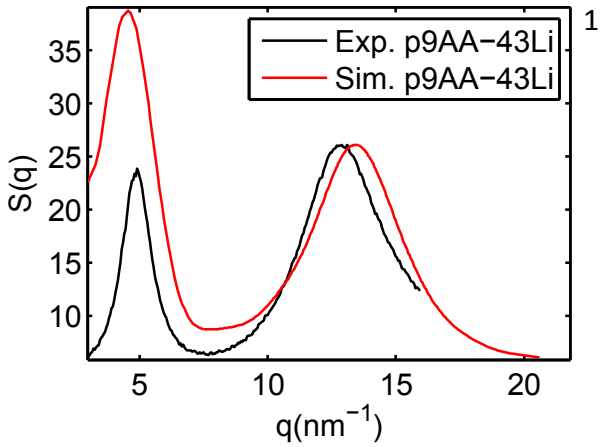




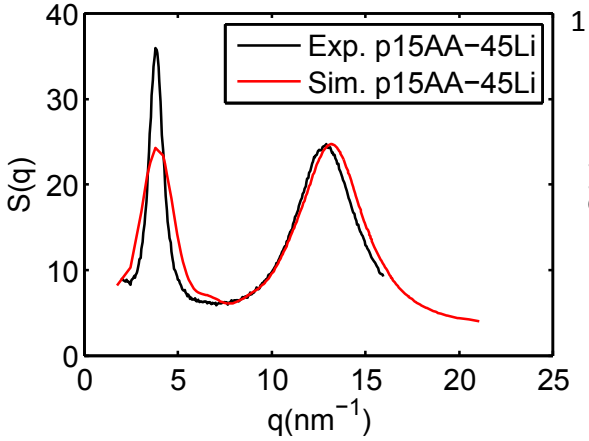
Cs^+

Mark Stevens
msteve@sandia.gov

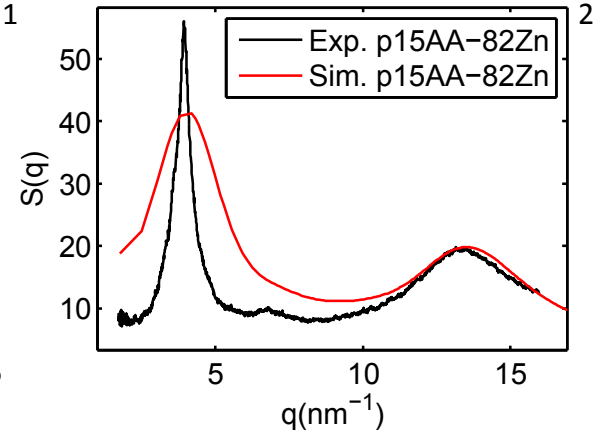
Direct Comparison



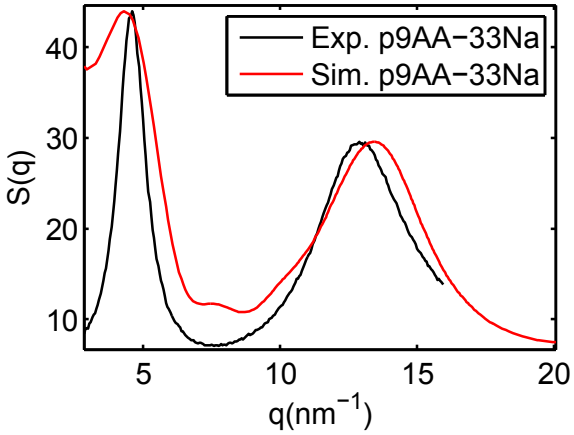
[1]



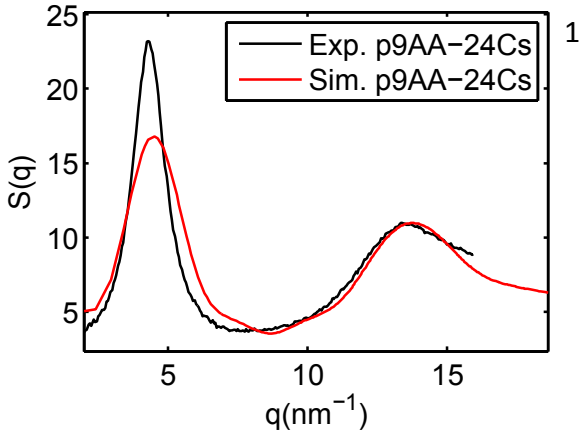
[1]



[2]



[1]



[1]

- 120°C, same neutralization
- S(q) scaled to match amorphous halo height

[1] Buitrago et al, sub to Macromolecules
[2] Seitz et al, JACS 132, p. 8165 (2010)

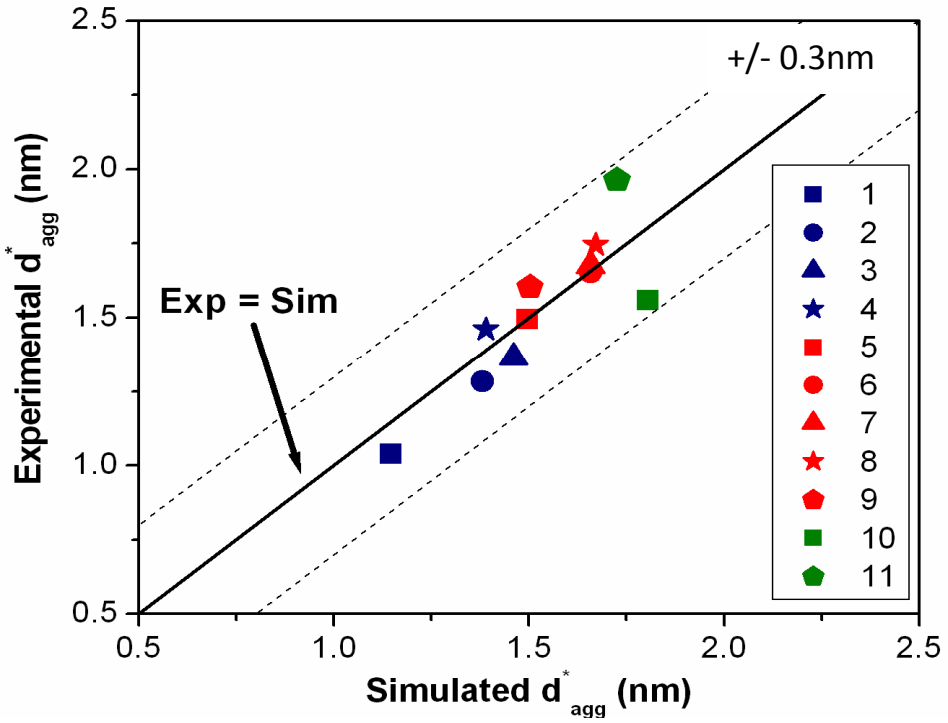
- excellent agreement in peak positions
- simulation ionomer peak broader

Mark Stevens
msteve@sandia.gov

Ionomer Peak Positions

simulation vs. experiment

$d^*_{agg} = 2\pi/q^*$



p9
(p9AA, 43%Li, 33%Na, 24%Cs)

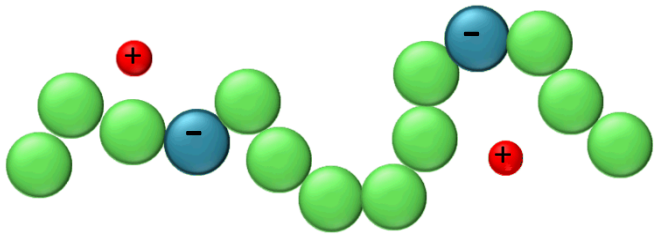
p15
(p15AA, 45%Li, 34%Na, 31%Cs, 82%Zn)

p21
(p21AA, 56%Zn)

Mark Stevens
msteve@sandia.gov

Coarse-grained Simulations

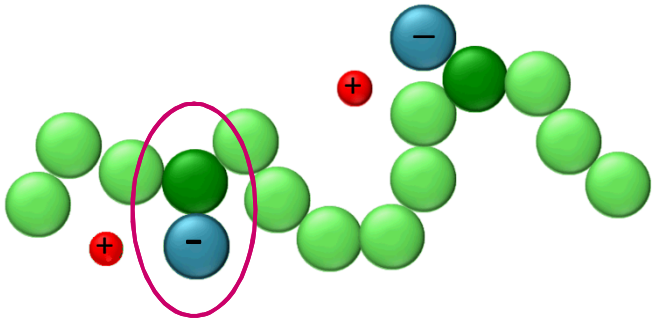
Ions in the polymer backbone:
"**ionenes**"



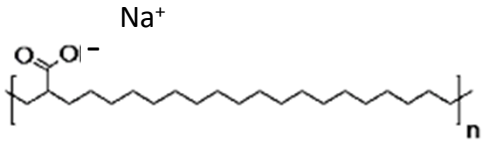
backbone beads per repeat unit

$N_{bb} = 7$

Ions pendant to the backbone:
"**pendants**"

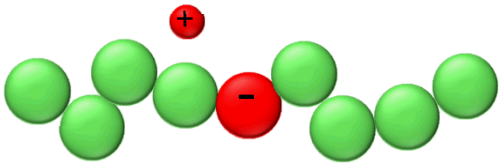


N_{bb} = 3, 5, 7, 9 (11)
1 bead ~ 3 C atoms
800 polymers
100% neutralization
counterion size = ½σ
bulk dielectric constant = 4
Bjerrum length = 35.7σ
10^8 time steps

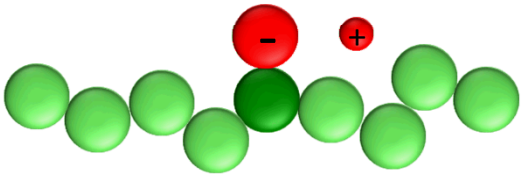


Mark Stevens
msteve@sandia.gov

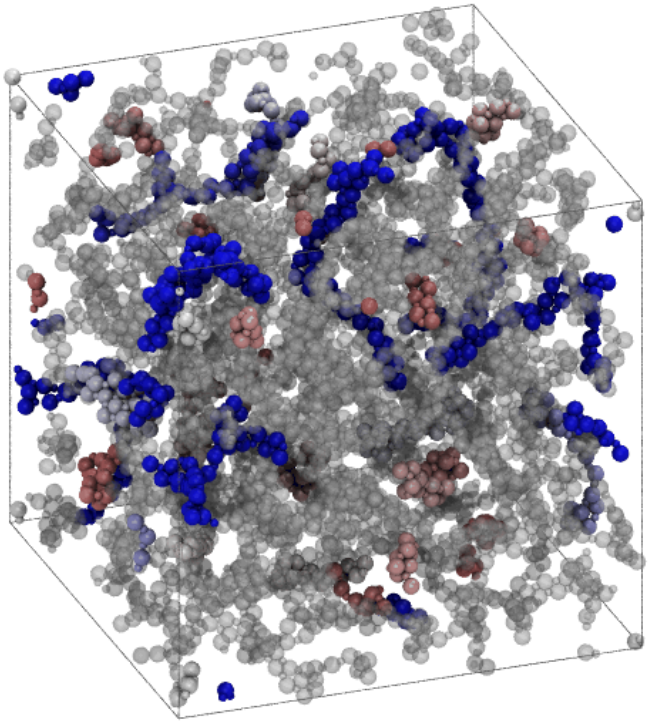
Aggregate Morphology: Architecture Matters



Ionenes: percolated

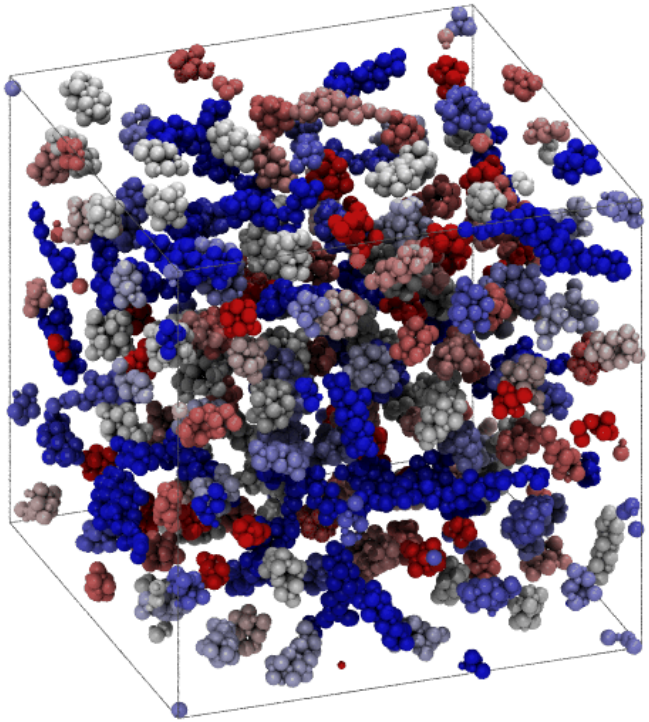


Pendants: not percolated



$N_{bb} = 9$

$\varepsilon_r = 4$



Small clusters → Large clusters

Only charged beads shown

Hall et al., *Phys. Rev. Lett.* (2011)

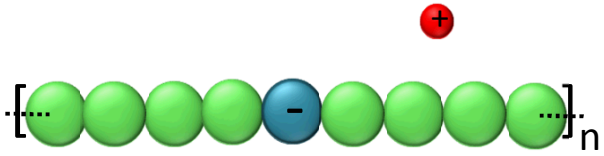
Mark Stevens
msteve@sandia.gov

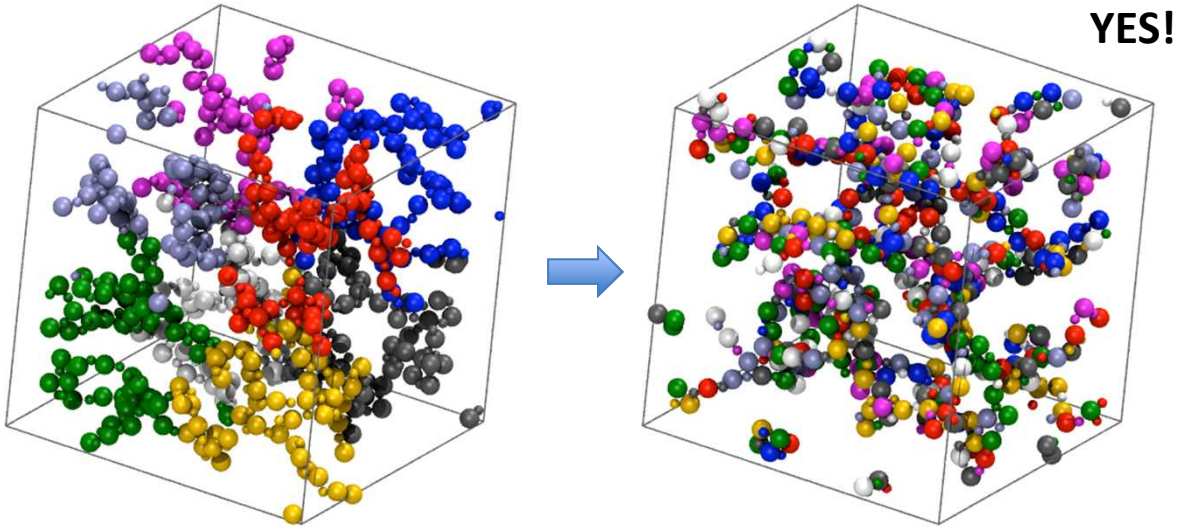
Cluster Dynamics

Is there any?

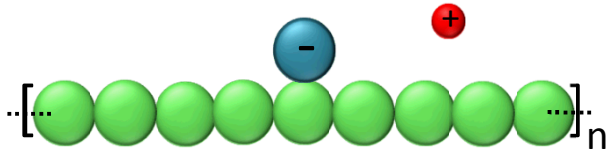
YES!

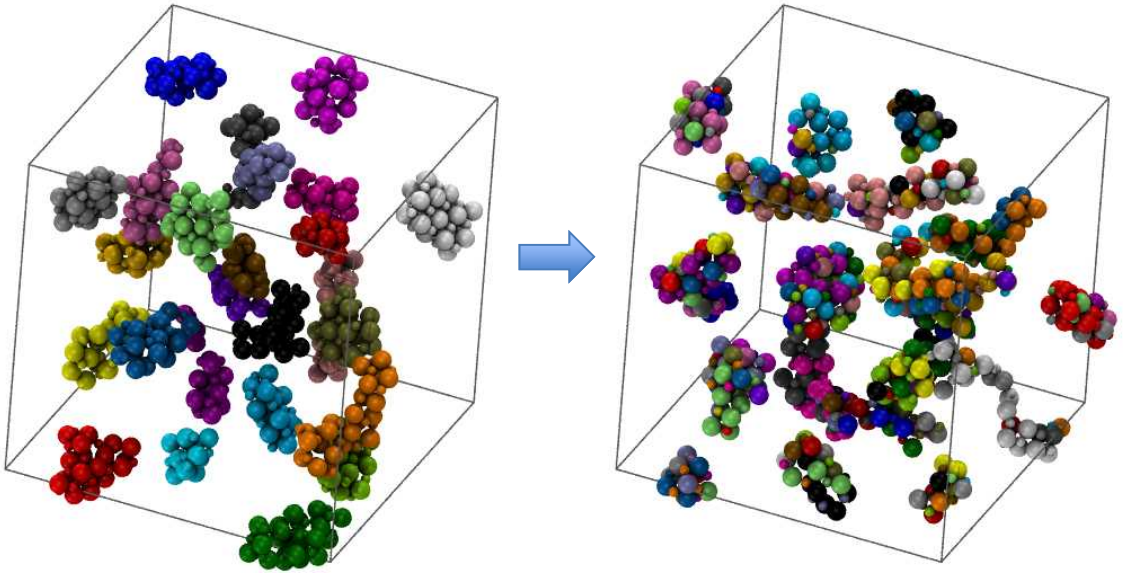
periodic ionenes, N_{bb}=9
colored by octant





periodic pendants, N_{bb}=9
colored by cluster

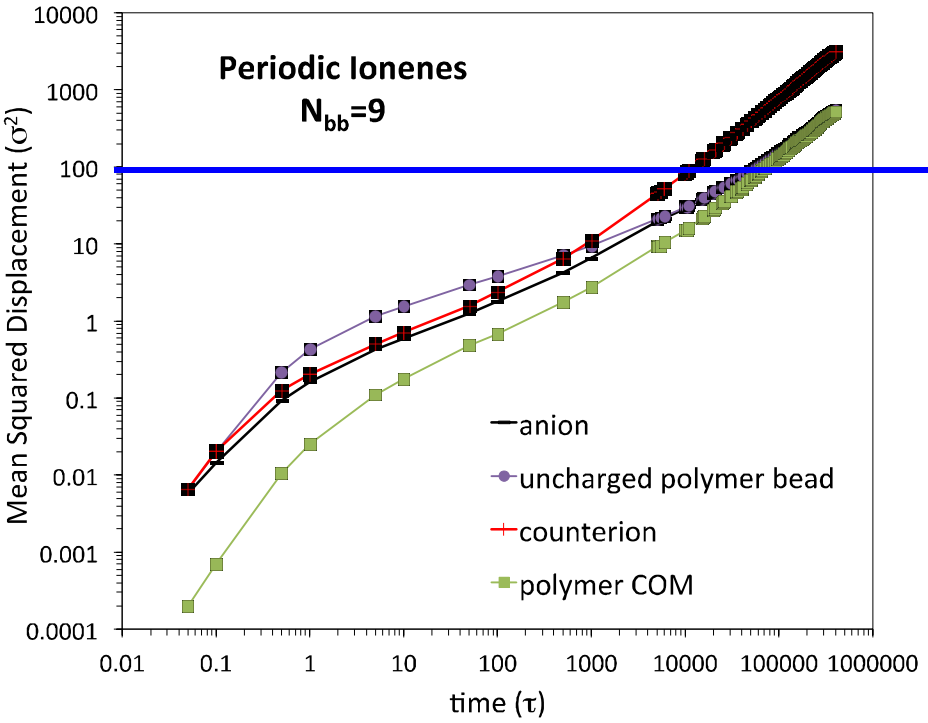


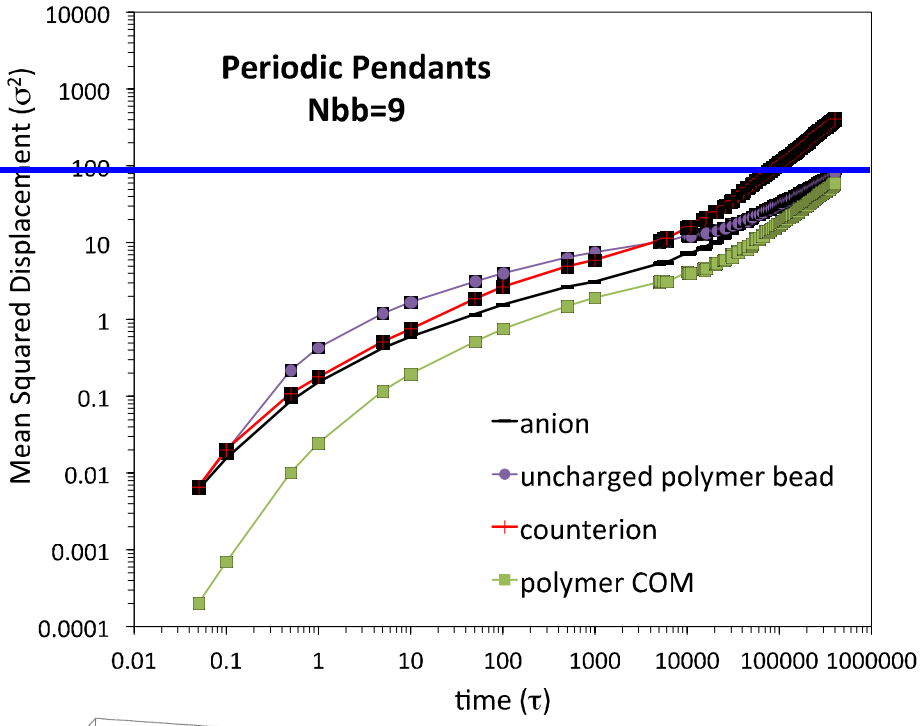


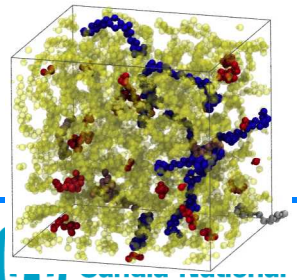
Mark Stevens
msteve@sandia.gov

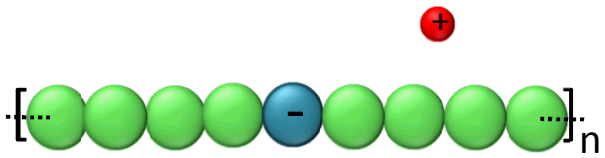
Mean Squared Displacements

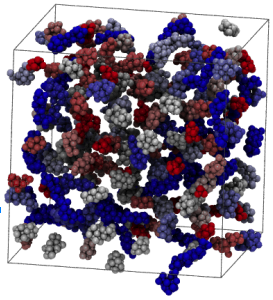
- We can reach the Fickian regime.
- Counterions in Ionenes (percolated) are faster
- Smaller N_{bb} is faster (not shown)

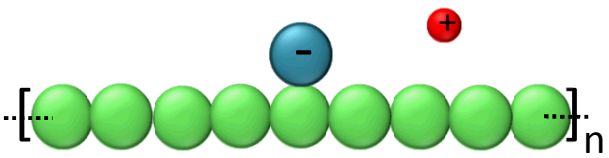










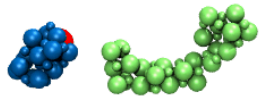


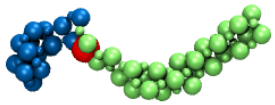
Mark Stevens
msteve@sandia.gov

Ion Trajectories

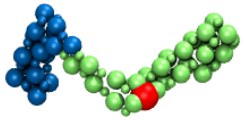
periodic pendants N_{bb}=9

2 separate clusters
Follow one counterion

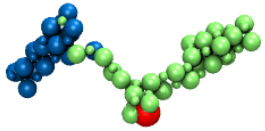


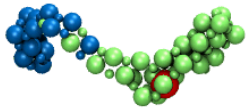


Clusters collide

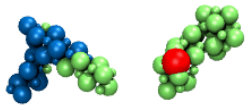


Ion has moved to other cluster.
Diffuses relatively fast within cluster.
NEVER separated from a cluster.





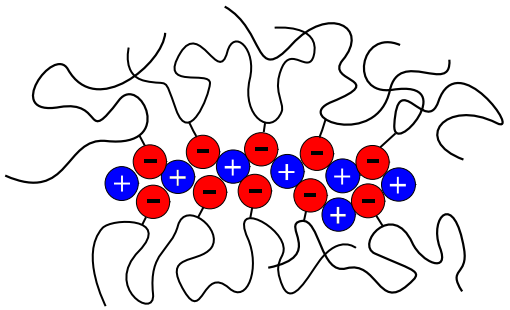
ions move by cluster rearrangment/collision



Clusters reform with ion moved

Mark Stevens
msteve@sandia.gov

The New Picture



- Aggregates are stringy
  - + – + – ordering
  - polymer backbone constraints
- Counterion influences structure
  - Na^+, Li^+: medium-sized, stringy aggregates
  - Cs^+: Percolated network
  - Zn^{2+}: small, isolated clusters
  - Small ion-O^- clusters are bridged by -OH and =O groups
- Neutralization level influences structure
  - Percolated structures tend to occur for high %N
- molecular architecture important
  - pendant vs ionene
  - isolated aggregates for pendants or large spacing
  - percolation for ionenes or short spacing
- **ion motion by aggregate rearrangment (distinct aggregates)**
- **ions diffuse faster in percolated morphologies**

Mark Stevens
msteve@sandia.gov

Exascale

Need faster computers to treat the atomistic dynamics of polymer systems

- adhesives & ionomers

Will need to use better and more expensive force-fields that commonly used now.

- polarizable

Interfaces are common in problems AND

they typically involve distinct types of materials with distinct treatments (e.g. FF)

Mark Stevens
msteve@sandia.gov

Acknowledgements

Acknowledgements
PNIPAM: Lauren Abbott (SNL)
Ionomers: Amalie Frischknecht, Dan Boltineanu, Christing Ting, Lisa Hall
Karen Winey (U Penn), Jim Runt (Penn St.)

Funding from LDRD and CINT/BES Facilities

Mark Stevens
msteve@sandia.gov

Mark Stevens
msteve@sandia.gov

Useful Info

Need to know:

- morphology
- relation between molecular architecture & morphology
- effects of morphology on ion transport
- understanding of ion transport mechanisms

Advice to experimentalist/engineer:

- morphology depends on counterion, neutralization, molecular architecture
  - Li is independently ion of choice
  - Cs, Zn are not good substitute probes
- maximize conductivity
  - percolated morphology preferred
  - maximize neutralization
  - ion in backbone better than pendant

Mark Stevens
msteve@sandia.gov

Publications

Atomistic

C. Buitrago, et al. Macromolecules 48, 1210 (2015).
D. Bolitineanu, et al. ACS Macro Lett. **2**, 206 (2013)
D. Bolitineanu, et al. *Macromolecules* **46**, 5381 (2013)
C.A. Lueth, et al. *J. Chem. Phys.* **140**, 054902 (2014)

Coarse-grained

Hall et al.,
Phys Rev Lett **106,** 127801 (2011)
J. Am Chem. Soc. **134**, 574 (2012)
Macromolecules, **45**, 8097 (2012)
Ting et al. *Macromolecules*, **48**, 809 (2012)

Mark Stevens
msteve@sandia.gov

Summary of Atomistic Simulations

Simulations resolve the ionomer peak.

Morphology:

- **stringy** (except maybe Zn)
  - not spherical as previously assumed
- **varies** with neutralization
- varies with anion type
- **percolation** occurs at large enough neutralization
- not well resolved in scattering
- ionomer peak due to interaggregate scattering
  - but can be isolated or percolated aggregates!

Trends

- larger aggregates as neutralization increases
- shorter aggregates as spacer length increases

Hydrogen bonding important in partially neutralized systems

Simulations match experimental S(q) well

Mark Stevens
msteve@sandia.gov