SAND2014-1341C

Ionic Aggregation and Dynamics in Ionomers: Insights from Molecular Simulation

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GRC on Colloidal, Macromolecular & Polyelectrolyte Solutions

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Sandia National Laboratories

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Ionomers

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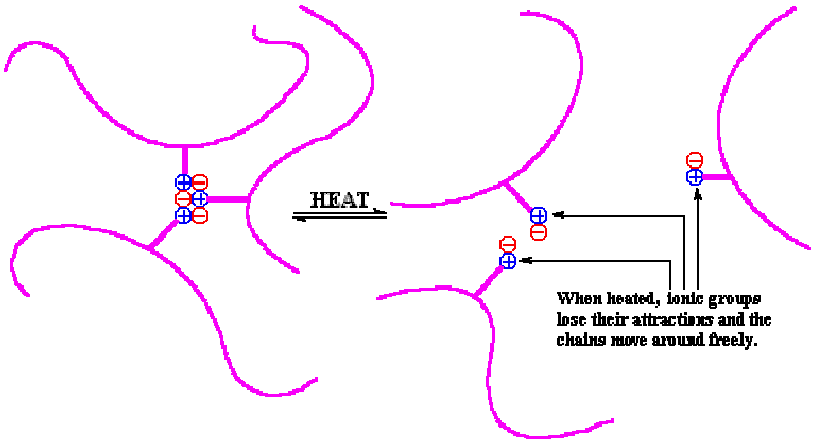
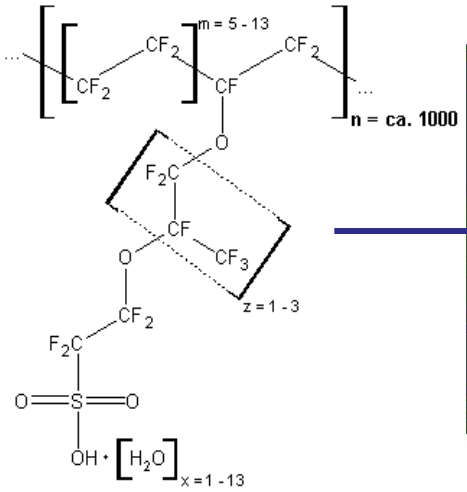
thermoplastic elastomers

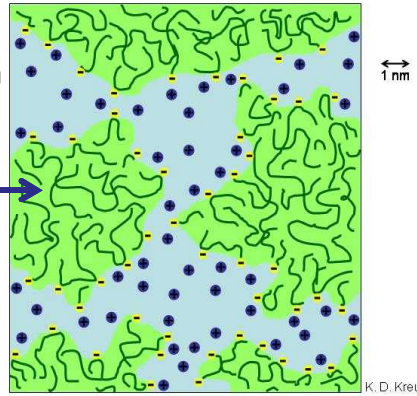


- low T: ionic aggregates behave like crosslinks
  - material is elastic
  - high strength
- high T: ionic aggregates break up
  - material flows (is a liquid)

ion-selective membranes typically in water

- water purification
- fuel cells





Possible Application: Batteries

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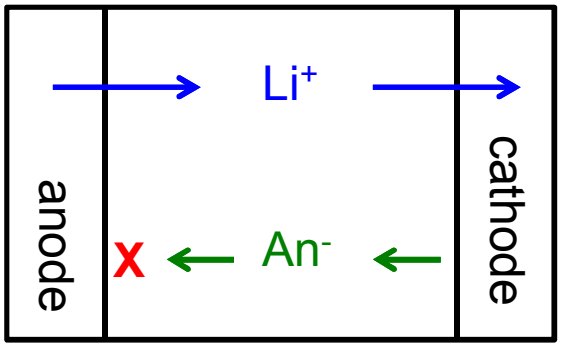
Issues with current electrolytes in Li-ion batteries:

- organic solvents
- PEO + lithium salts + solvent
  - need containment
  - flammable!

- solvent free PEO + salt
  - conductivity dominated by anions
  - salt concentration at electrodes
  - extra heating



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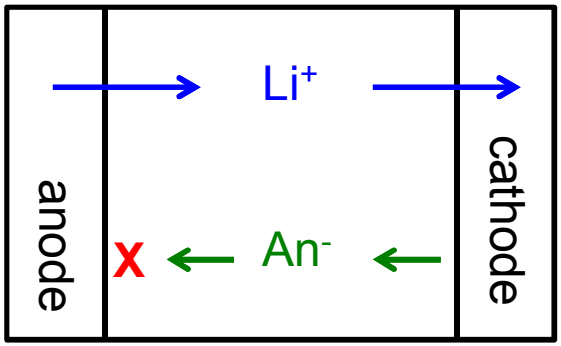

ionomers as next generation electrolytes?

- safer: no solvent
- serve as electrolyte & separator
- less packaging
- improved electrochemical stability
- higher efficiency: single ion conductors

Ionomers: Polymers + Ions

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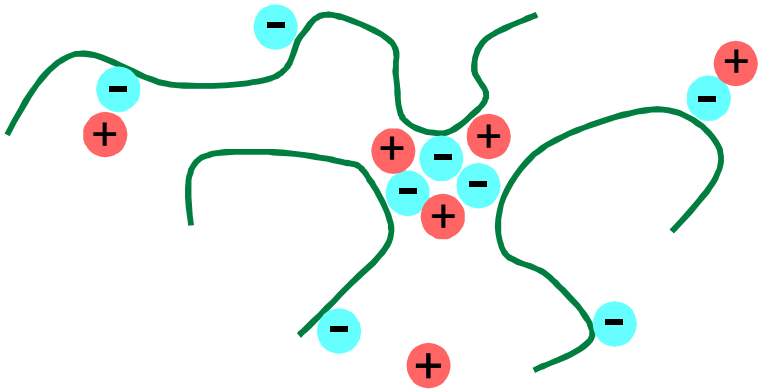
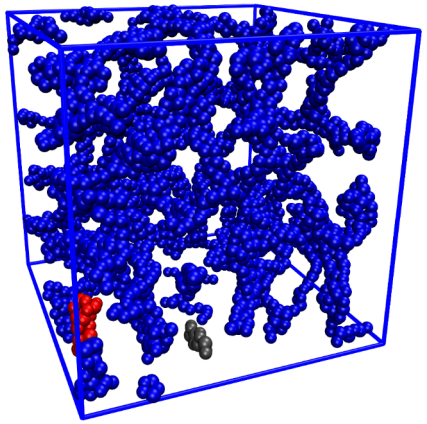
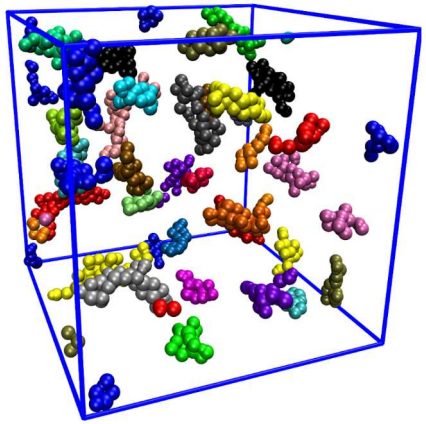
often form ionic aggregates





- electrostatic forces favor aggregates
- polymer entropy limits size



do aggregates lead to low conductivity?

Current Ionomer Conductivities

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- conductivity too low
  - needed for Li-ion batteries: ≥ 10^{-4} S/cm at room temp.
  - Li salt + solvent: ≈ 10^{-2} S/cm
  - gel polyelectrolytes: 1-3 10^{-3} S/cm
  - ionomers: often < 10^{-5} S/cm

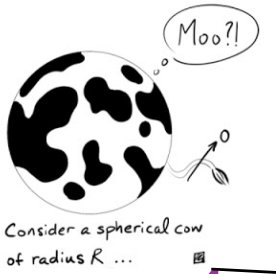
- why?
  - few mobile ions (ion pairs instead)
  - often get ionic aggregates

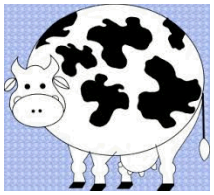
Need for electrochemical apps:

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

Simulations can help!

Modeling (Simulating) Polymers





string model
- good for theory
- mesoscales

coarse-grained model
- used a lot in simulations
- intermediate length, time scales

atomistic model
- chemically specific
- limited in time, length scales

Precise Ionomers

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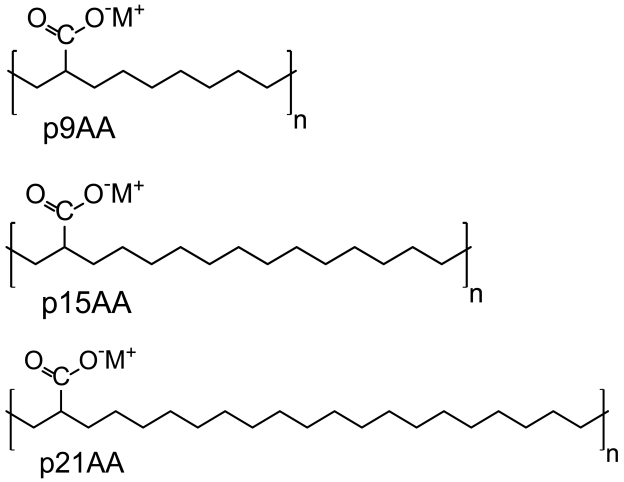
Acyclic Diene Metathesis (ADMET) Precise Copolymer



precise polymers:

- acid group every 9, 15, 21 carbons
- swap H for Zn^{2+}, Li^{+}, Na^{+}, Cs^{+}
- nomenclature: pxAA-y%M

Morphology: Li-neutralized pAA

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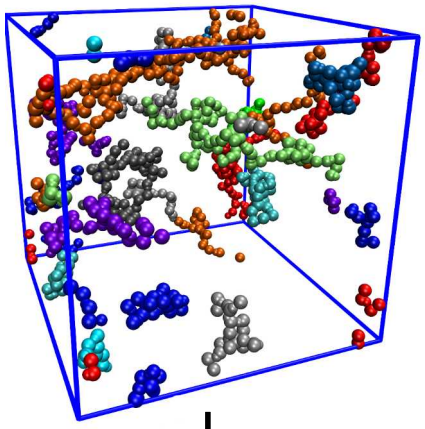
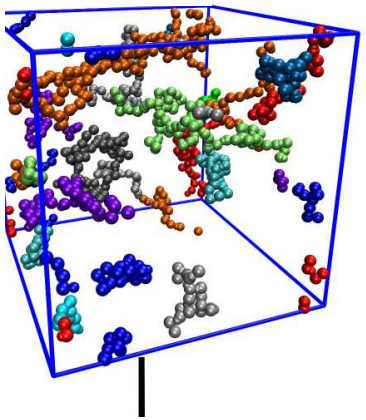
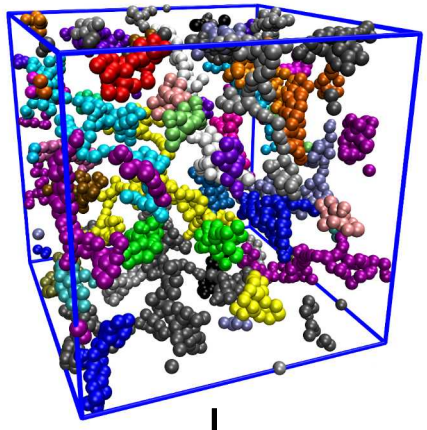
coloring by cluster

p9AA-10%Li

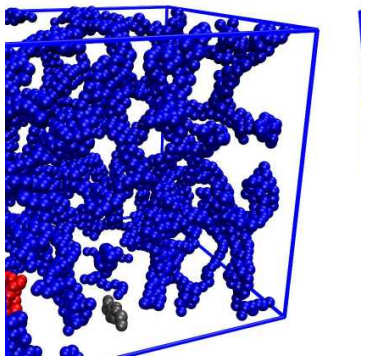




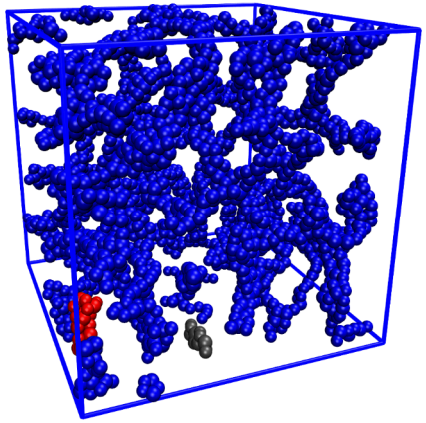
p9AA-43%Li



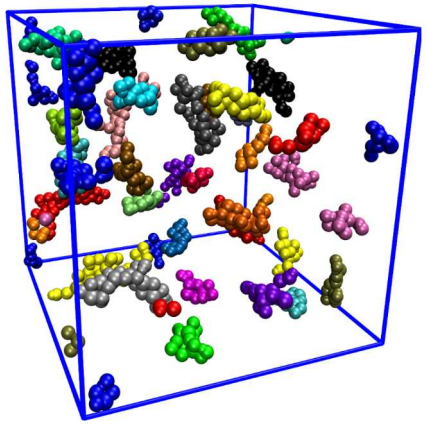
c. p9AA-100%Li
FP



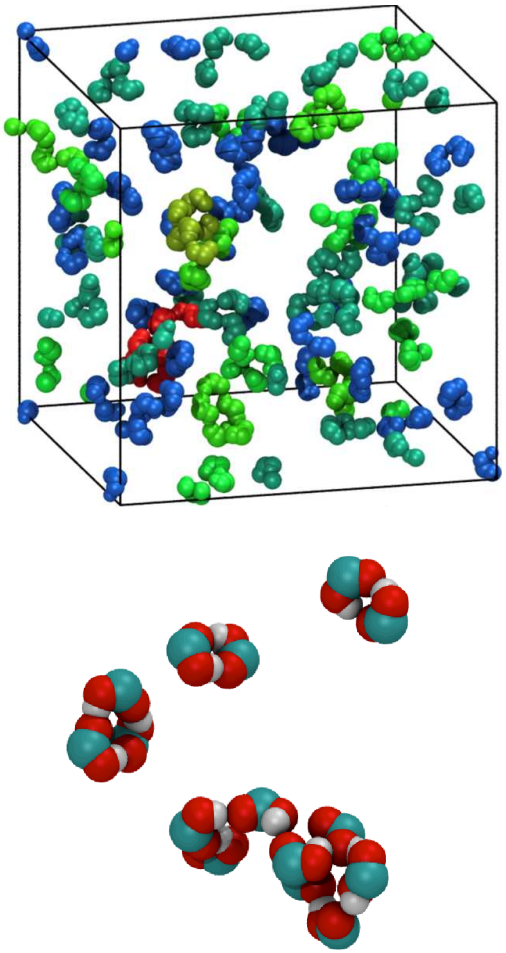
p9AA-100%Li

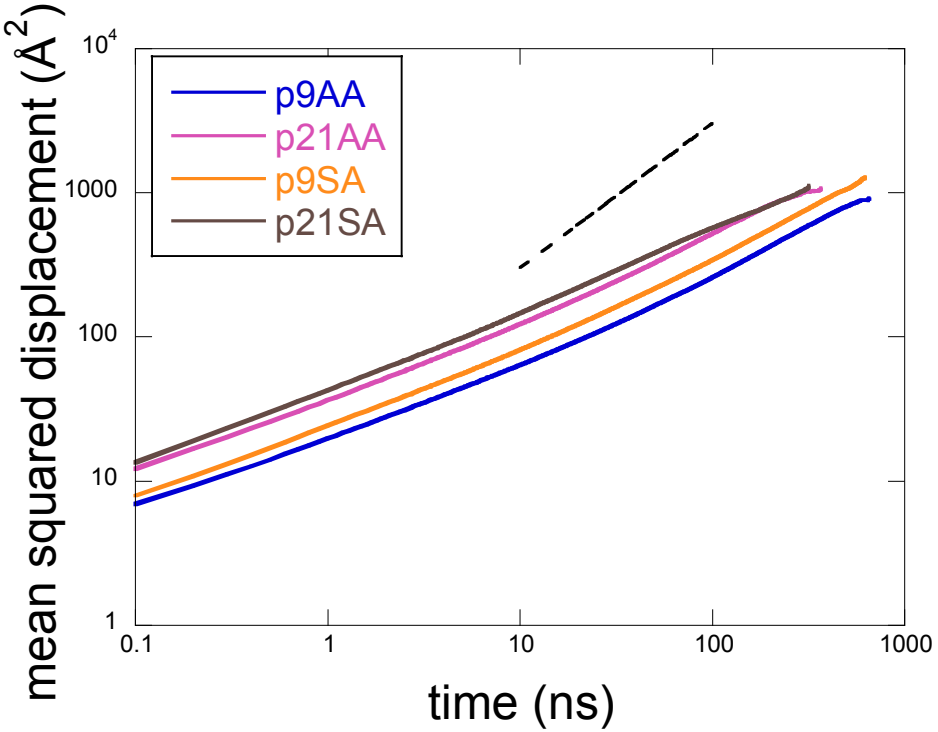


p21AA-43%Li



Dynamics in Acid Copolymers





- H's move about 31 Å during simulation
- not yet diffusive

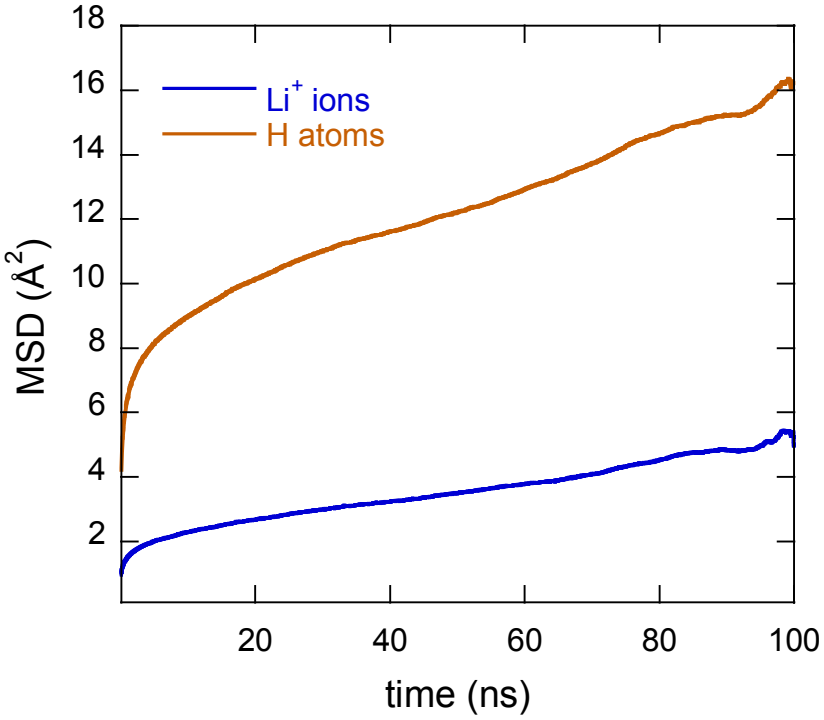
$$\langle r^2 \rangle = Dt$$

Lueth, C. A., Bolintineanu, D. S., Stevens, M. J. & Frischknecht, A. L. *J Chem Phys* **140,** 054902 (2014).

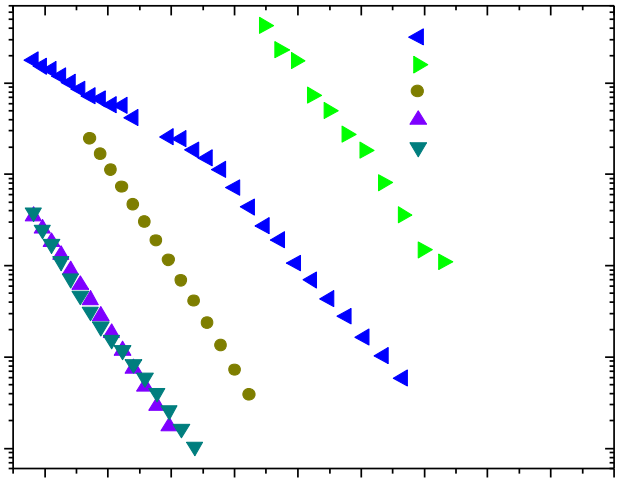
Dynamics in Ionomers

p9AA-43%Li

last 100 ns of 500 ns simulation
very slow!

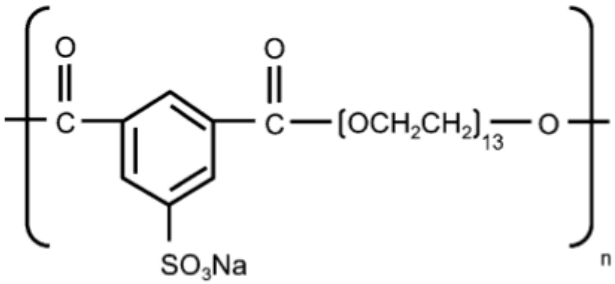


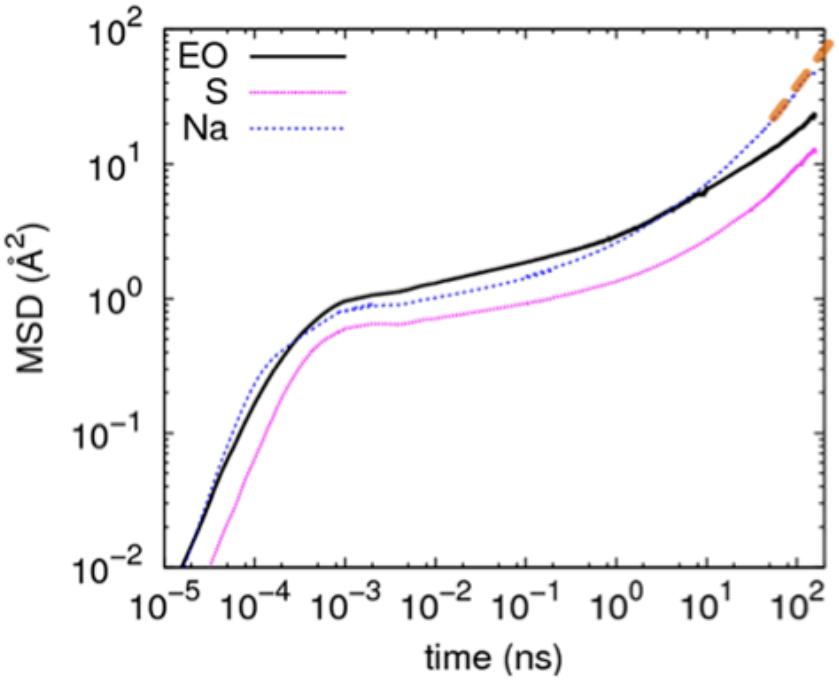
conductivity by DRS



J. Runt, H. Choi, et al.

A Faster Ionomer





Lin, K.-J. & Maranas, J. K. *Macromolecules* **45,** 6230–6240 (2012).

Coarse-Grained Simulations

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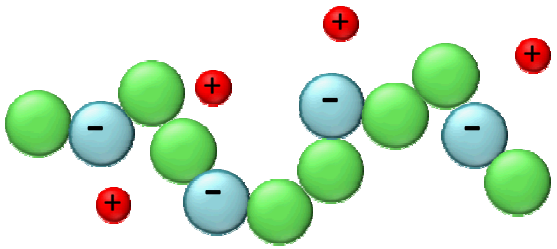
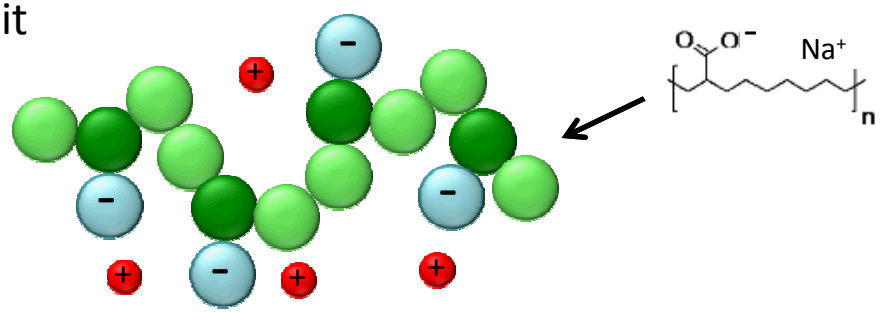
Ions in the polymer backbone:
"**ionenes**"



backbone beads per repeat unit

$N_{bb} = 3$

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



N_{bb} = 3, 5, 7, 9 (11)
800 polymers
100% neutralization
bulk dielectric constant = 4
counterion size = ½σ
Bjerrum length = 35.7σ

10^8 time steps

$$\ell_B = \frac{e^2}{4\pi\varepsilon_0\varepsilon_r kT} = 35.7\sigma$$

$$R_g \approx 3.1 - 3.3\sigma$$

Ionomer MD Simulations

repulsive LJ interactions + FENE springs ...

+ Coulomb interactions

$$U(r) = \frac{q_1 q_2}{4\pi\epsilon_0\epsilon r}$$ ε = 4

+ temperature

NVT ensemble: Langevin thermostat

$$f_i = -m_i\Gamma\nu_i + W_i(t)$$

noise *W* sets temperature

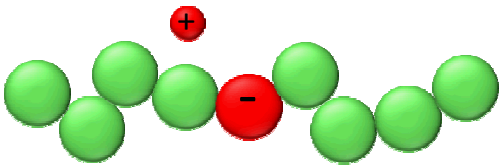
- 800 chains of 35-36 beads
- 4-12 charges per chain
- 1 cation per charged bead (anion)

- equilibrate for 10^7 timesteps
- collect averages for 4×10^7
- 1M CPU-hours ≈ 325 days on 128 cores

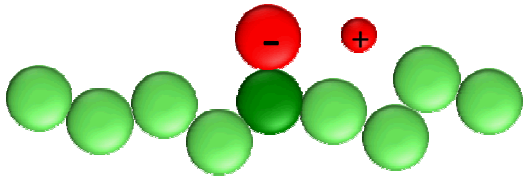
LAMMPS: open source MD code from Sandia
http://lammps.sandia.gov/

2,816 nodes / 22,528 cores

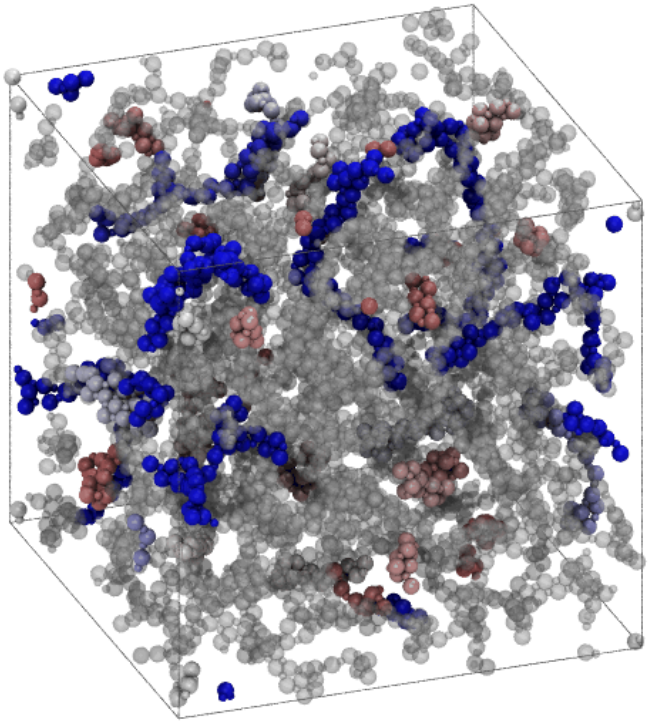
Aggregate Morphology: Architecture Matters



Ionenes: percolated

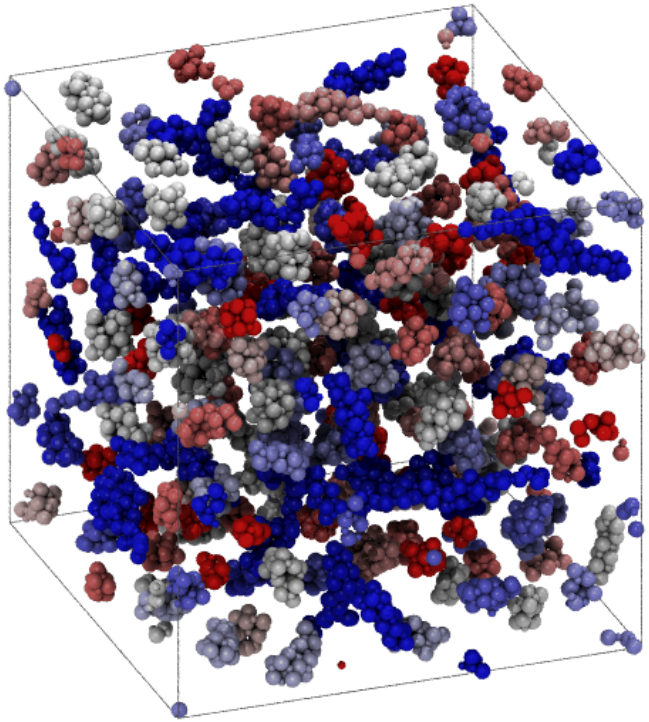


Pendants: not percolated



$N_{bb} = 9$

$\varepsilon_r = 4$



Small clusters → Large clusters

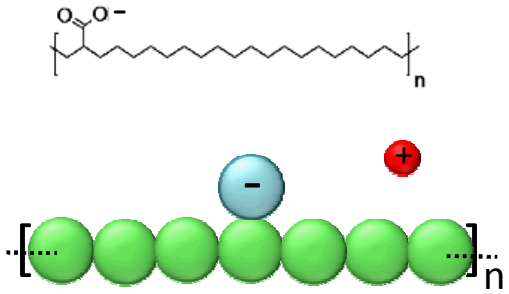
Only charged beads shown

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

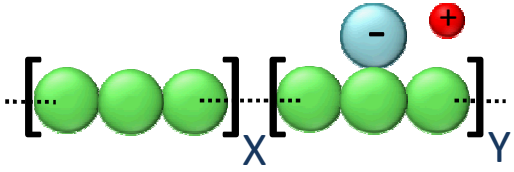
Randomly Spaced Ionomer Model

- random block
  - mimic ROMP
- fully random
  - mimics typical random polymerization

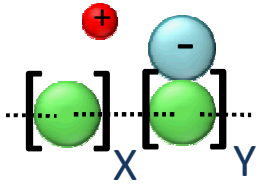
Periodic



Random Block Copolymer



Fully Random Copolymer



connect blocks randomly

vary X/Y

N_{bb} = Number of **b**ackbone **b**eads per charged bead

Aggregate Morphology: Random vs. Periodic

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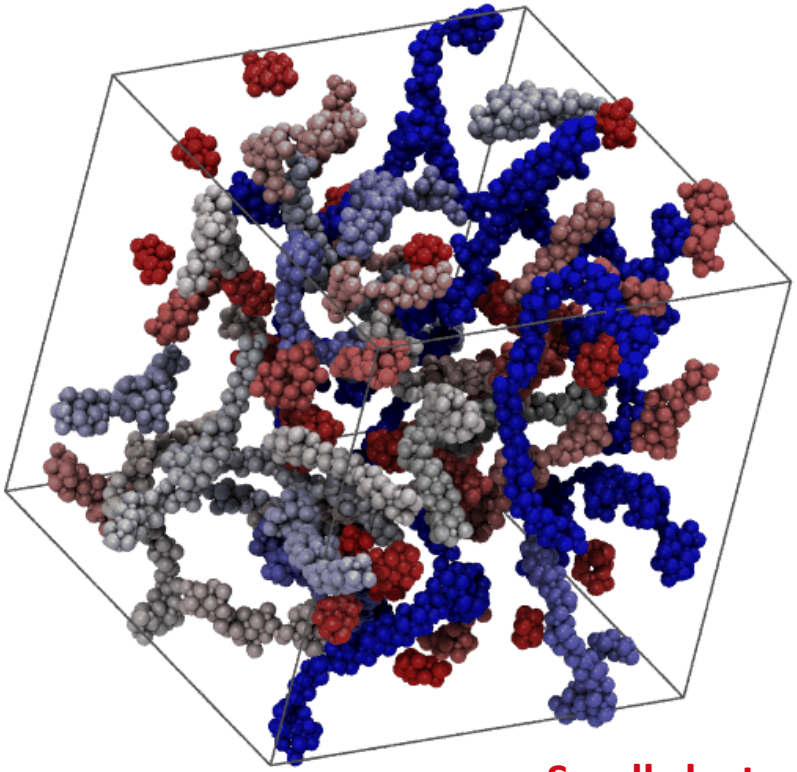
Random Block Copolymer
Pendants: stringy, large clusters

Mean cluster size 87

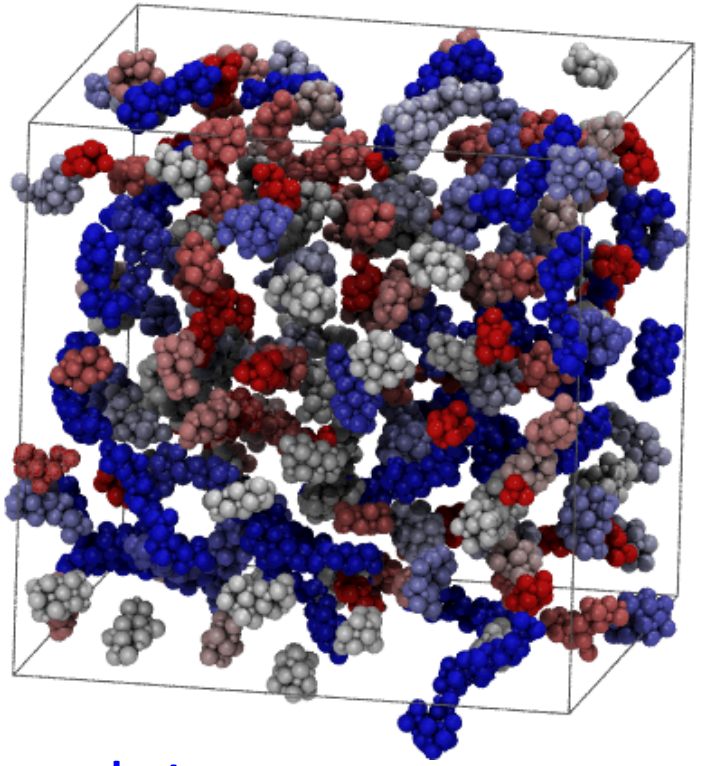


$\varepsilon_r = 4$

$N_{bb} = 9$

Periodic Pendants:
narrow cluster size distribution

Mean cluster size 31

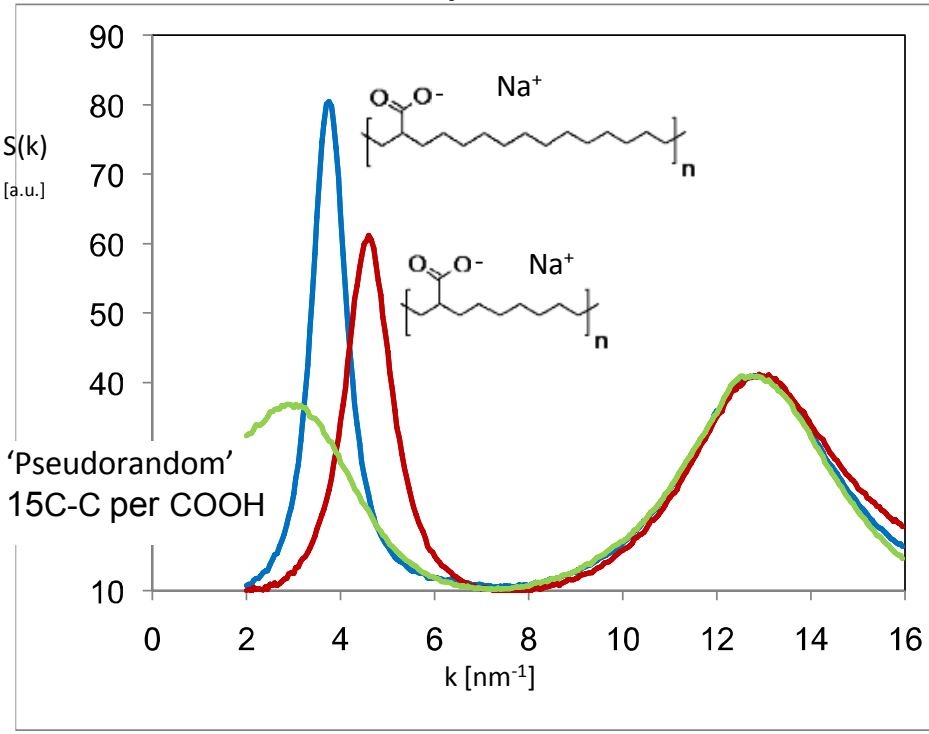


Small clusters → **Large clusters**

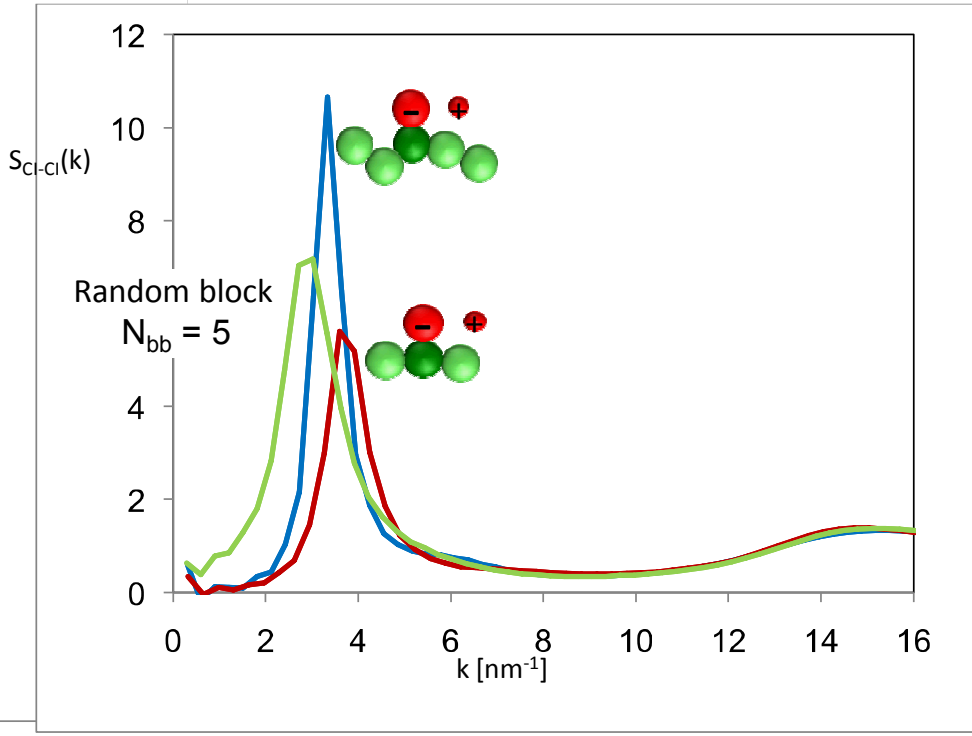
CG MD: Comparison to X-ray Scattering

- Experimental/Simulation Agreement
  - Peak location similar
  - Increasing spacing moves peak to left
  - Random spacing moves and broadens peak

Experiment



Simulation



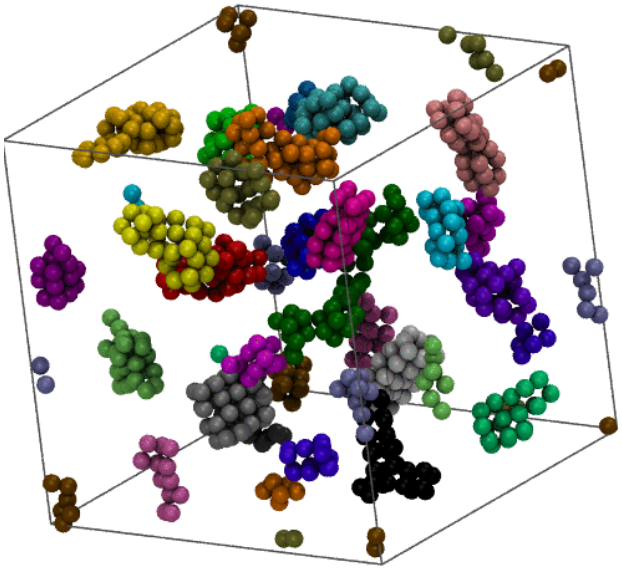
Hall et al., *J. Am Chem. Soc.* (2012)

Cluster Dynamics

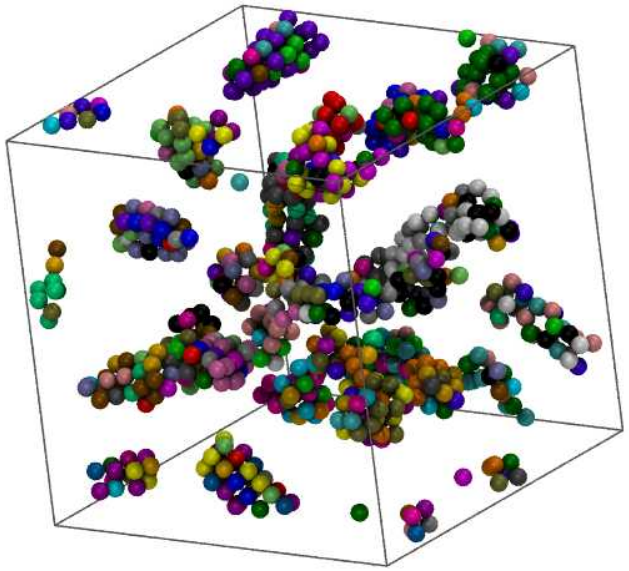
Is there any?

Color distinct clusters by different color

Start



Finish (10^7 steps later)

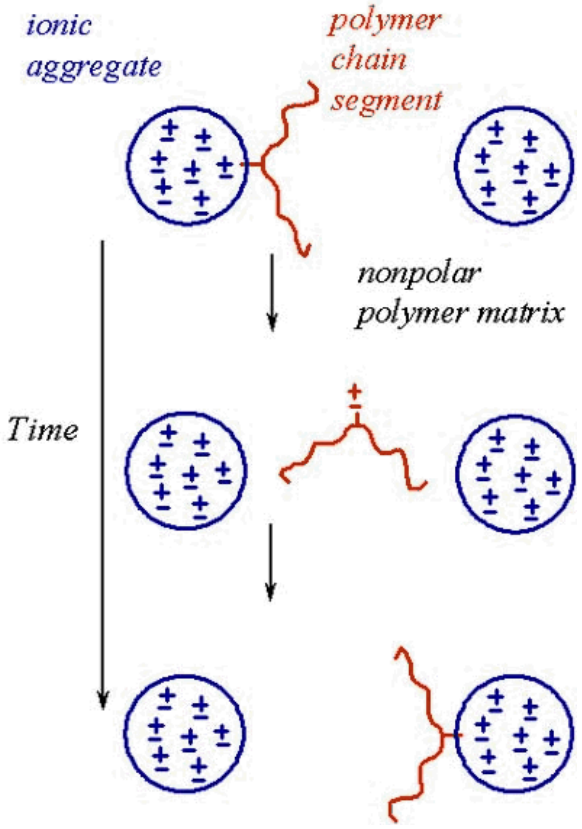


Ions move.

Historical View of Dynamics

- requires traversing low dielectric polymer matrix
- large activation energy barrier
- ion **pairs** “hop” between aggregates

this is SLOW



http://www.princeton.edu/cbe/people/faculty/register/group/research/ionomers/ionomer-melt-rheology-and/

Ion Trajectories

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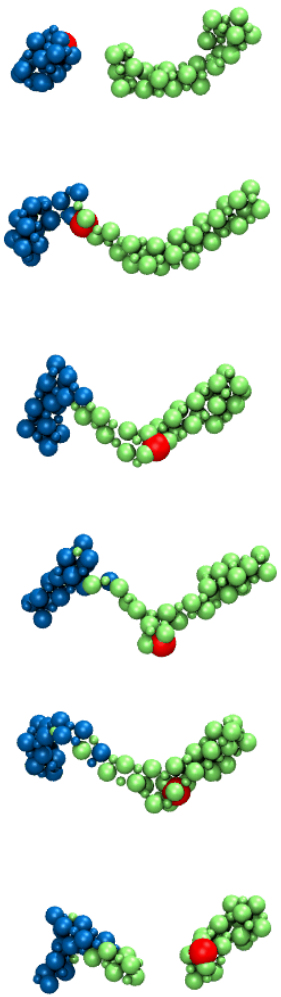
periodic pendants N_{bb}=9

2 separate clusters
Follow one counterion



Clusters have collided

Ion has moved to other cluster.
NEVER separated from a cluster.

Clusters reform with ion moved

ions move by cluster rearrangment/collision

Energies and Cluster Dynamics

+ – pair energy (contact) is 48 kT.

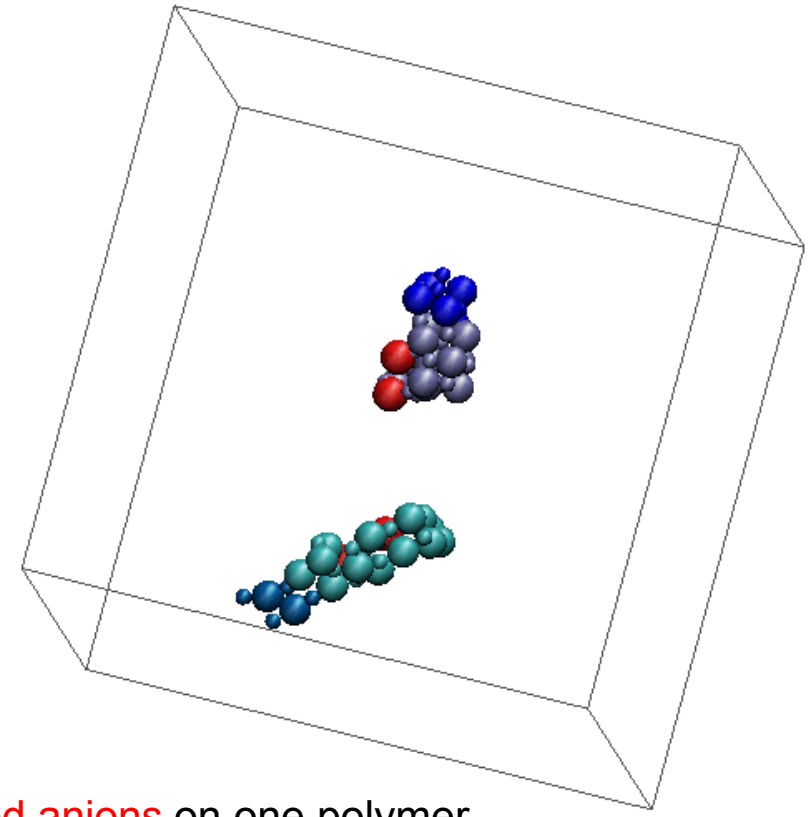
pairs are not likely to separate.

energy to split a cluster is much less
ideal, 2D crystallite has a separation energy of
only 20 kT:

simulations show clusters are flexible (they're liquids after all) and the energies will be less than these crystallite calculations.

ions move a lot within a cluster

Pendant (discrete clusters)



Red anions on one polymer.

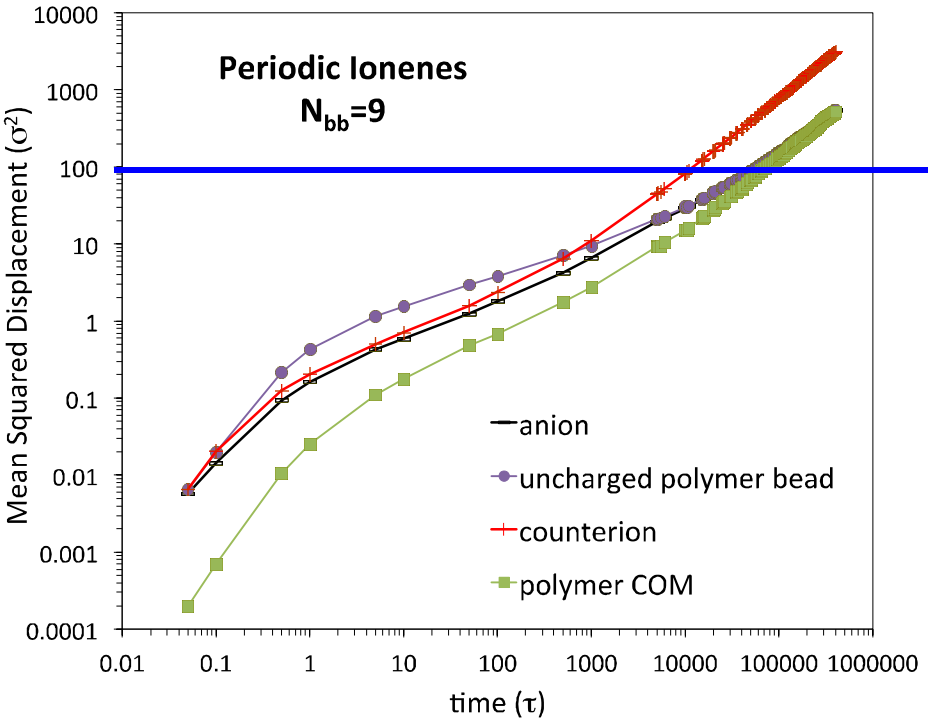
Blue ions initially within 3σ of red anions.

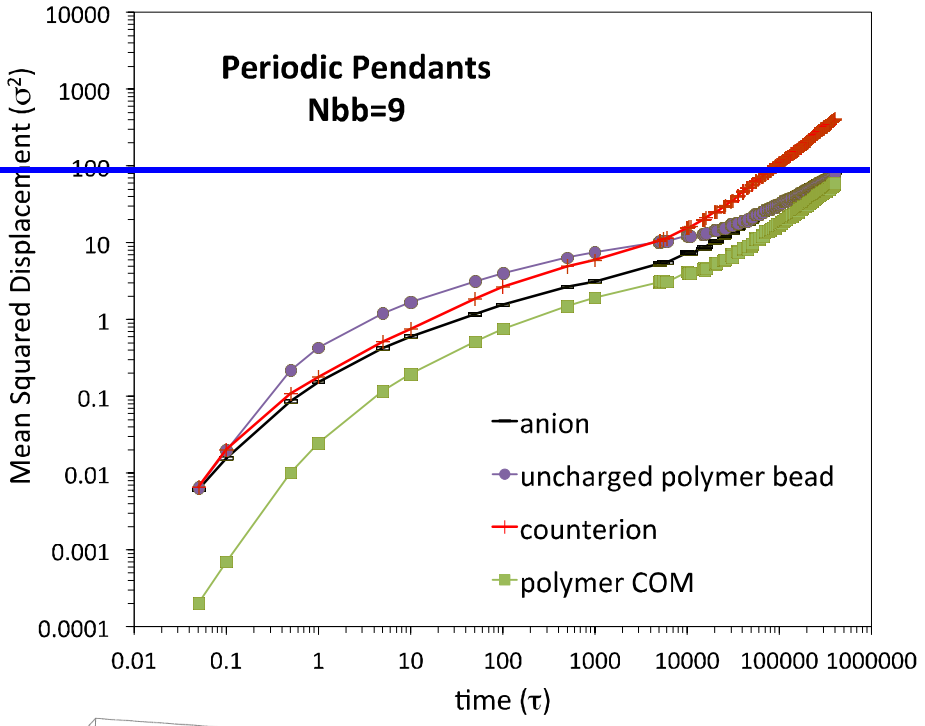
Other ions which temporarily come within 3 σ are transparent.

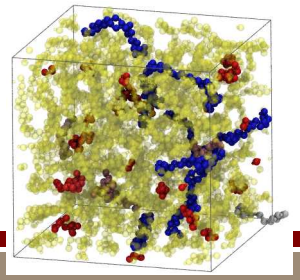
5000 τ X million time steps

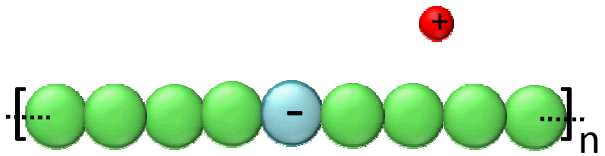
Mean Squared Displacements

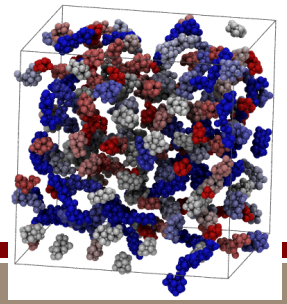
- Ionenes, pendants similar at short times
- Pendants slower but qualitatively similar at long times

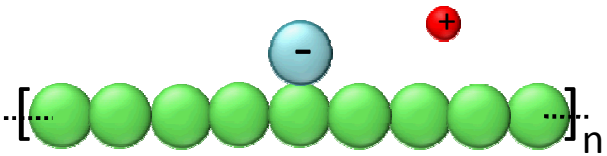








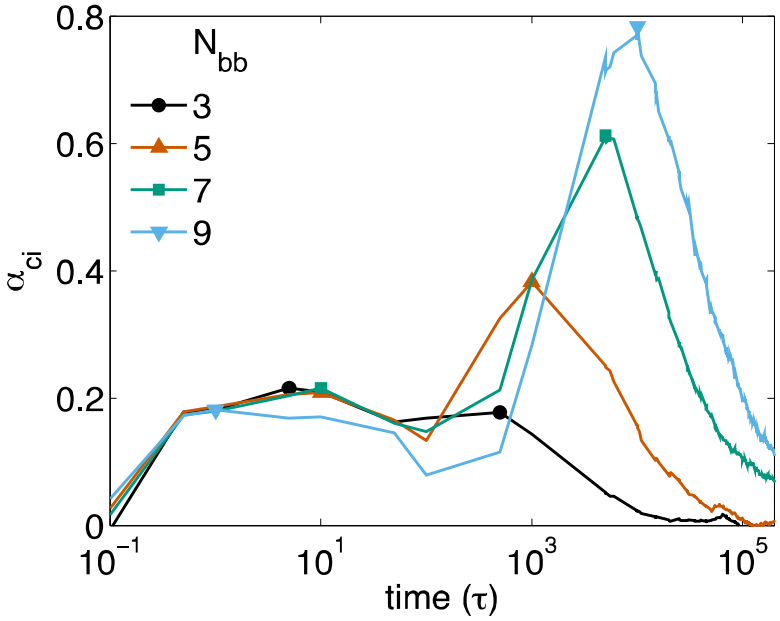




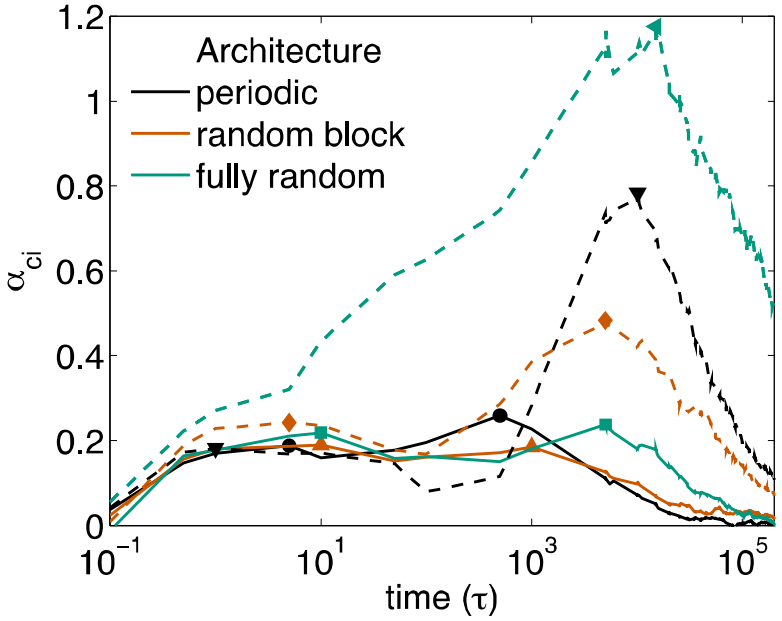
Ion Dynamics

non-Gaussian parameter $$\alpha(t) = \frac{3\left\langle (r(t))^4 \right\rangle}{5\left\langle (r(t))^2 \right\rangle^2} - 1$$

cations in periodic pendants



cations for N_{bb} = 9

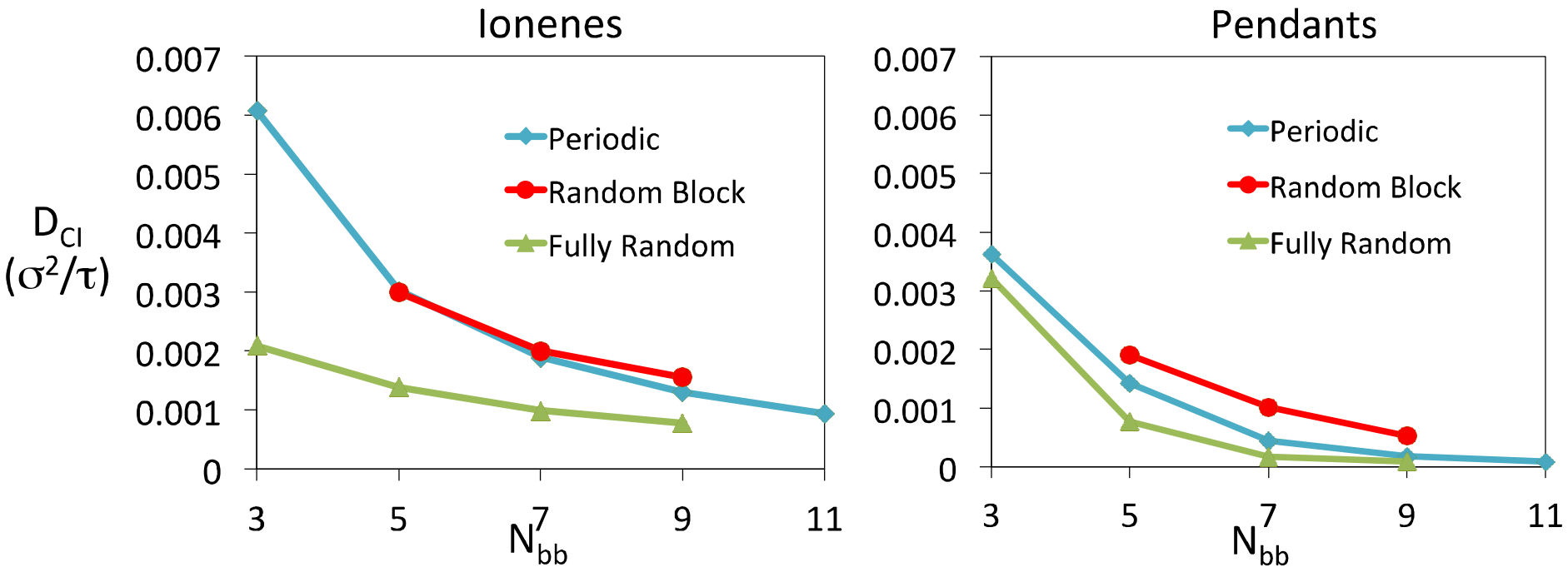


indicative of 2 time scales:

- local motion in clusters
- slower rearrangment between clusters

Counterion Diffusion Constants

- Ionenes conduct better than pendants
- Greater concentration of ions increases diffusion
- Blocky random copolymerization increases diffusion



$\varepsilon_r = 4$

Hall et al., *Macromolecules* (2012)

Static Electric Field

add force $F_x = qE_x$ to each ion

how strong a field should we add?

electrostatic force $$\frac{F}{kT\sigma} = -\frac{q_i q_j}{r^2}\frac{\ell_B}{\sigma}$$

LJ units: $|q| = 1$, $kT = 1$, $\sigma = 1$; $\ell_B/\sigma = 35.7$

at contact, $r = 0.75\sigma$: $F = -63/kT\sigma$

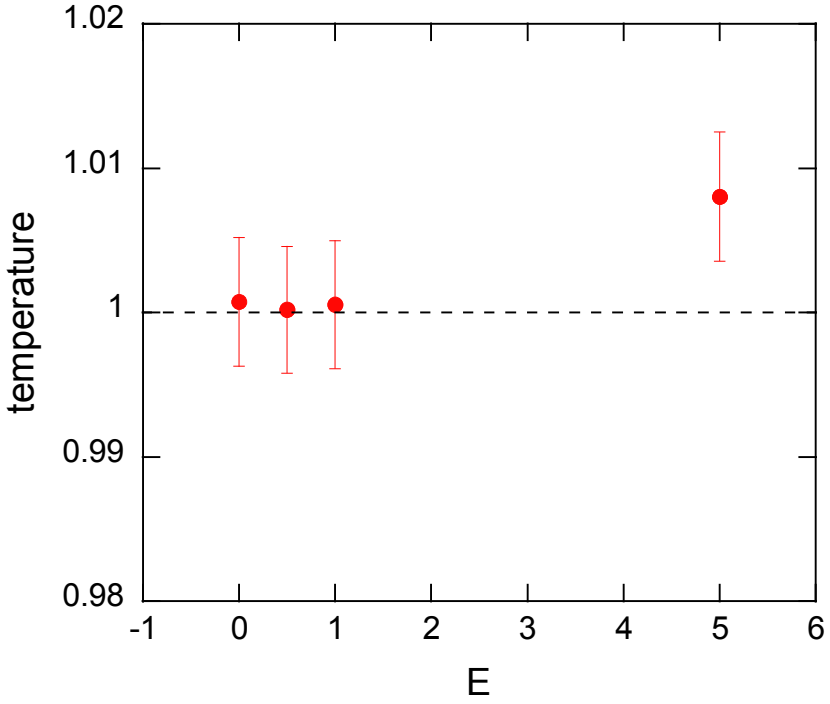
for field $$E^* = \frac{kT}{q\sigma} = 1$$ $F = 1/kT\sigma$

rough estimate in real units:
σ = 0.4 nm, T = 298K, E = 0.8 V/nm = 8x10^6 V/cm

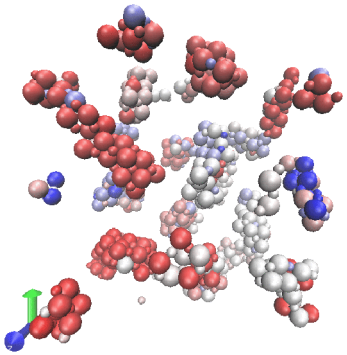
Check Field Strengths

turn off thermostat in field direction

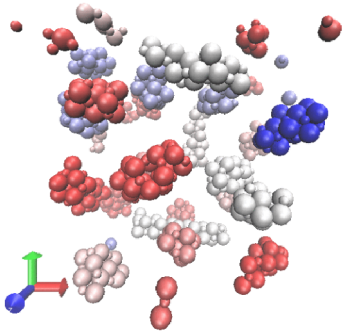
set $T^* = \frac{k_B T}{\epsilon_{LJ}} = 1$



Effects on Clusters

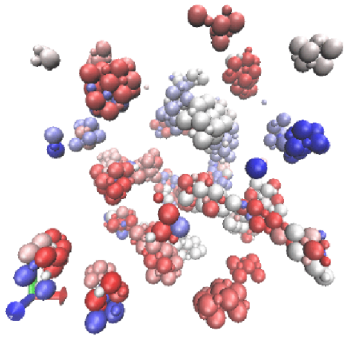


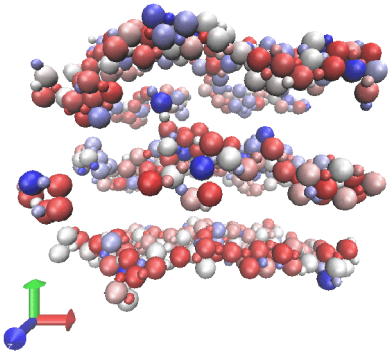
E'='0'



aZ er'2.585'x'10^{6}τ'

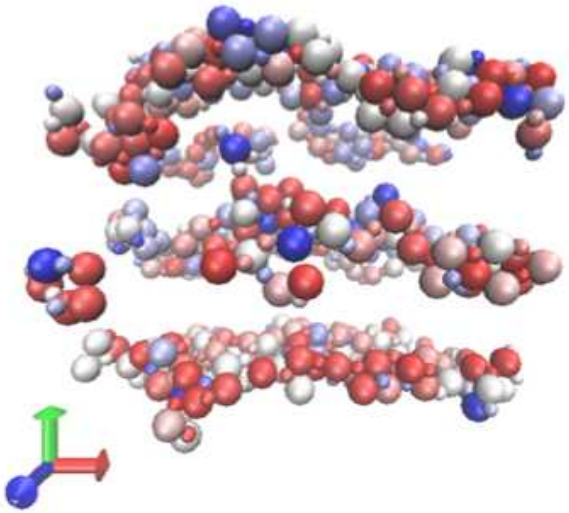
E'='1.0'



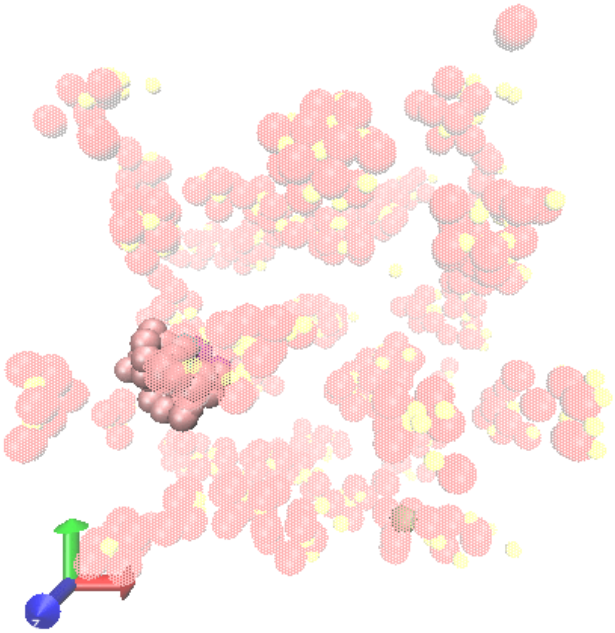


E'='5.0'

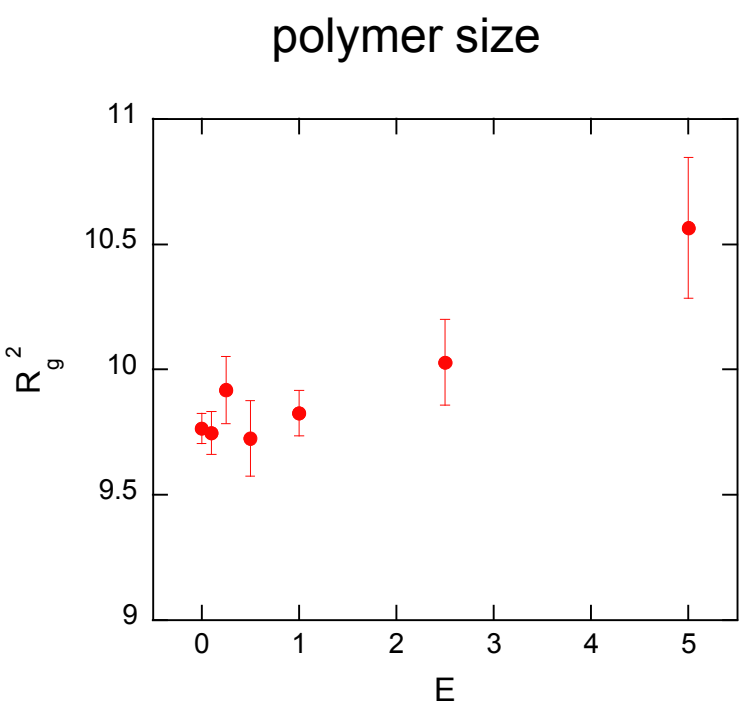
Aggregates Align in High Fields

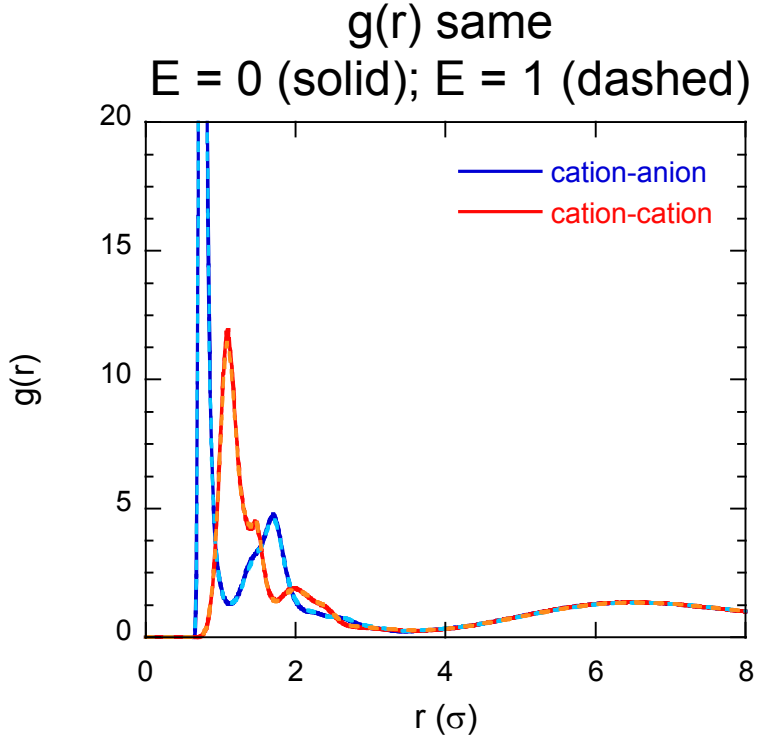


E = 5.0



Effect of Field on Structure

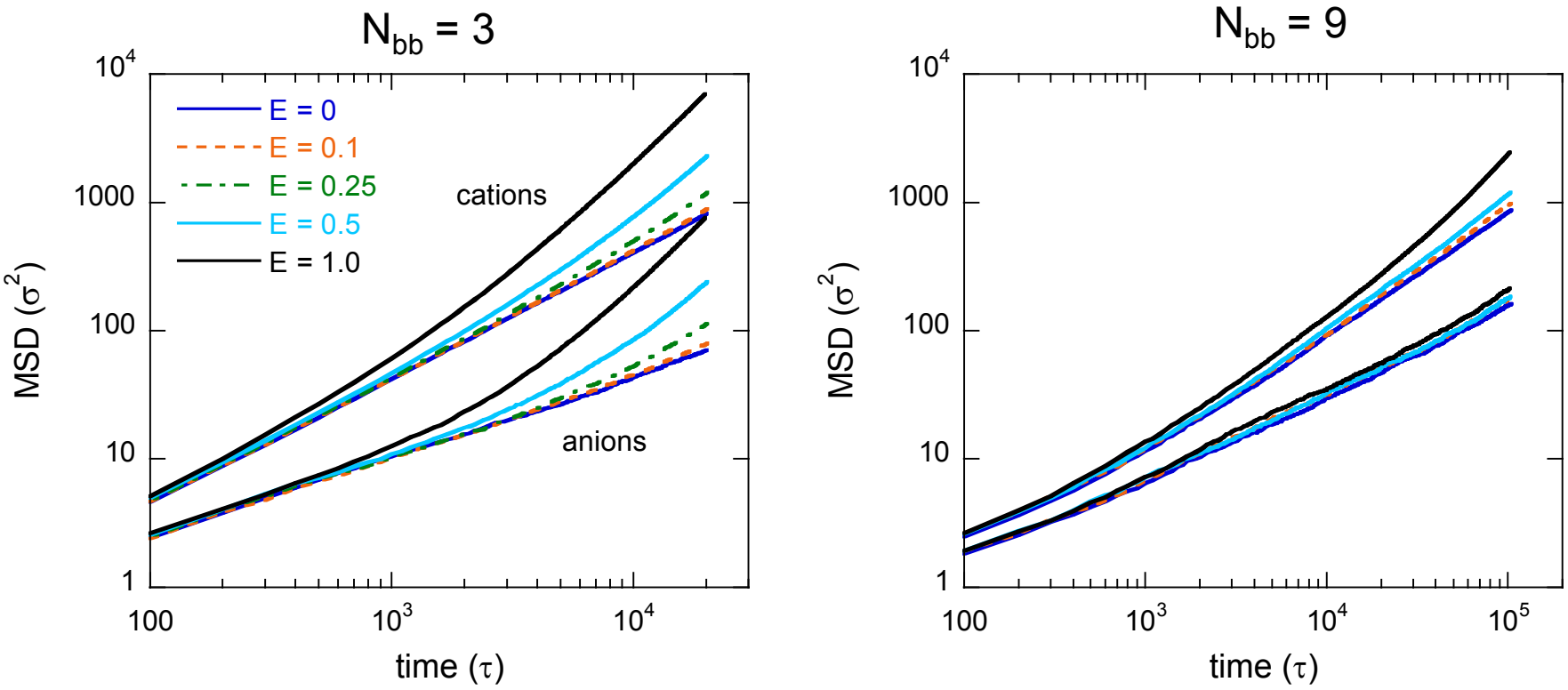




no effect for E ≤ 1

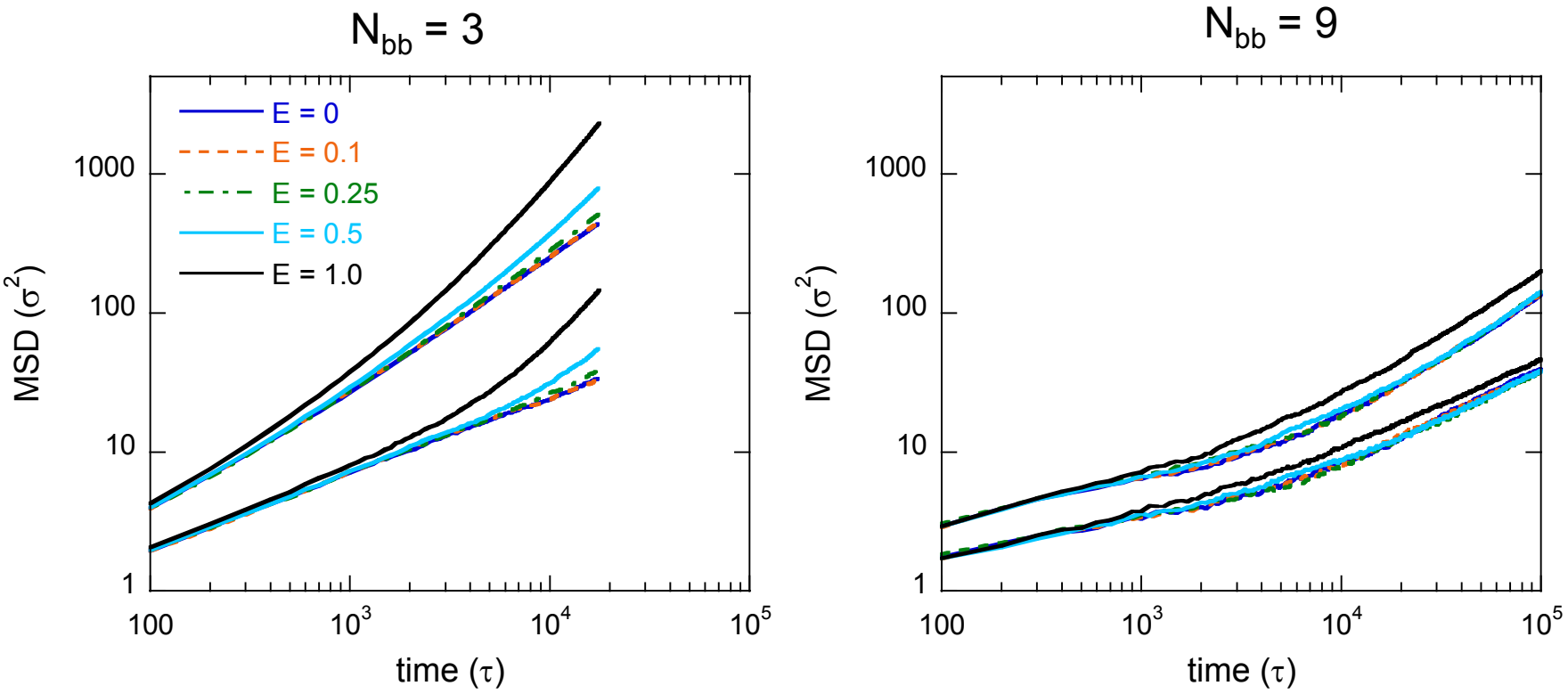
Mean-Squared Displacements

ionenes



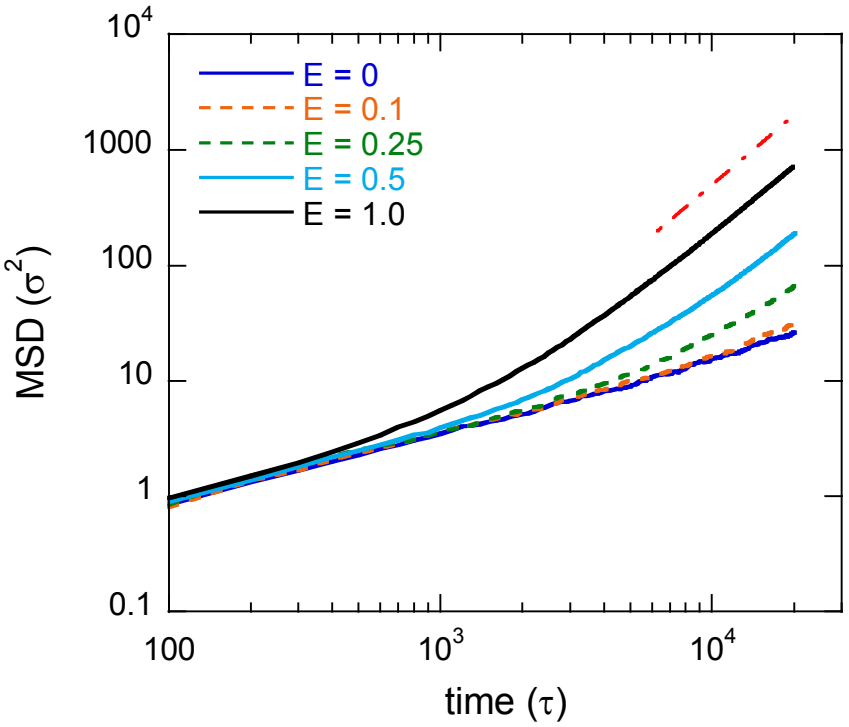
Mean-Squared Displacements

pendants

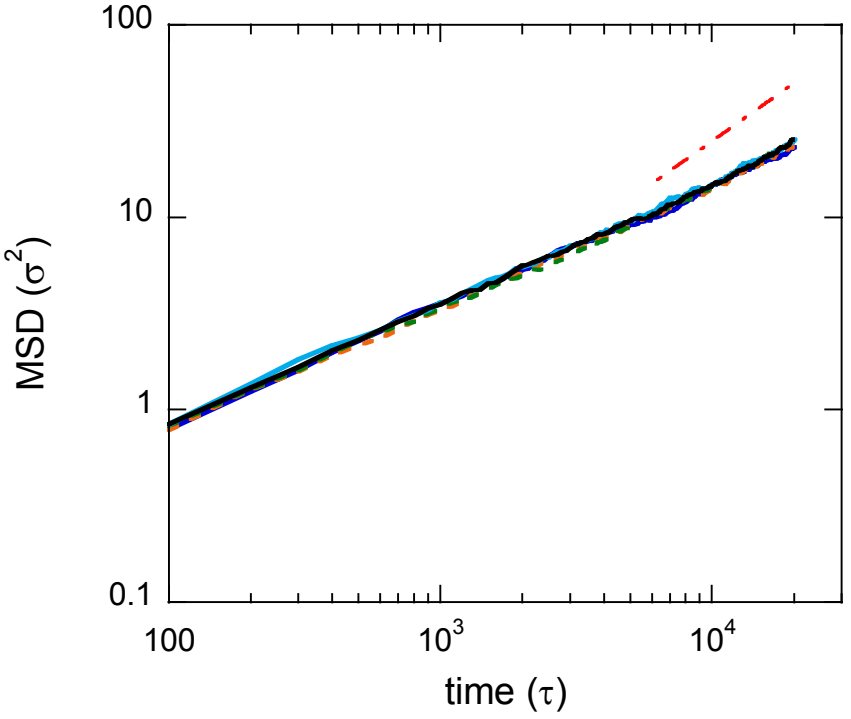


Directional MSDs

in field direction



perpendicular to field

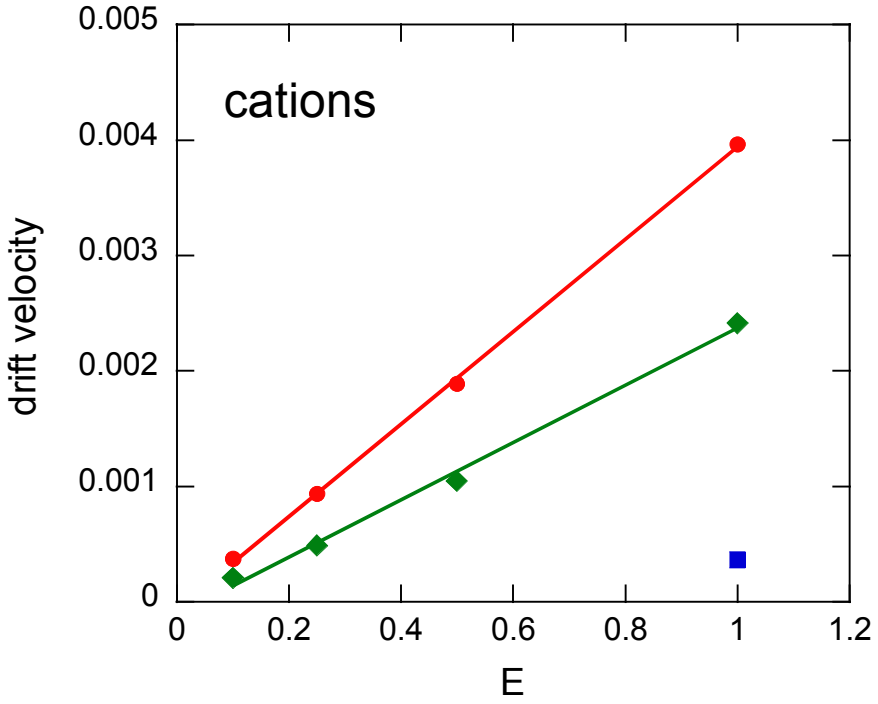


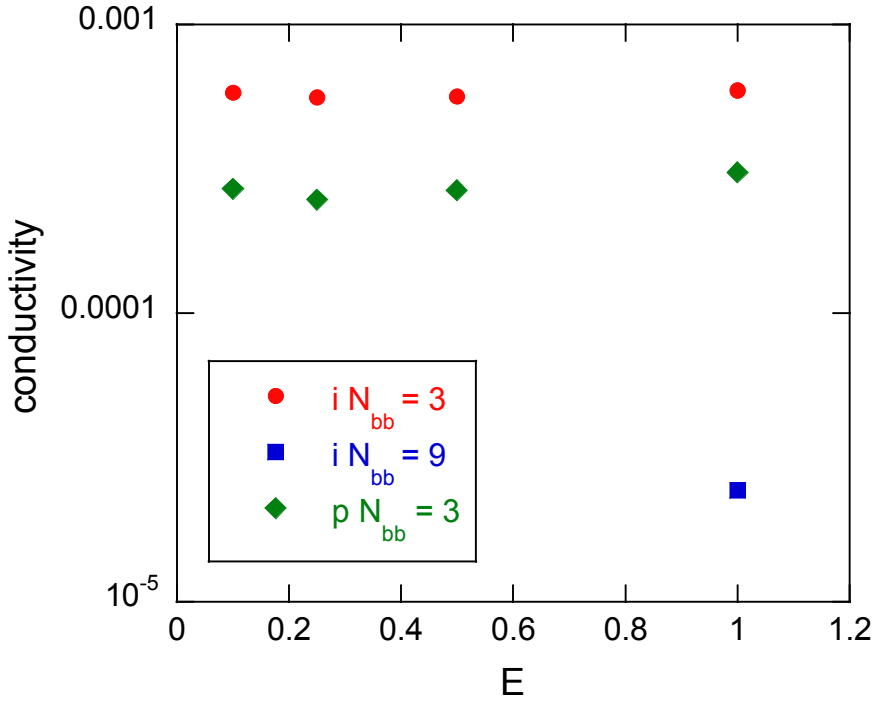
drift velocity: $\langle x_E^2(t)\rangle - \langle x_0^2(t)\rangle = \langle v_x^2\rangle t^2$

Conductivity

ion mobility: $\mu_i = \langle v_{x,i} \rangle / E$

conductivity: $\lambda = \rho e(\mu_+ - \mu_-)$





Nernst-Einstein

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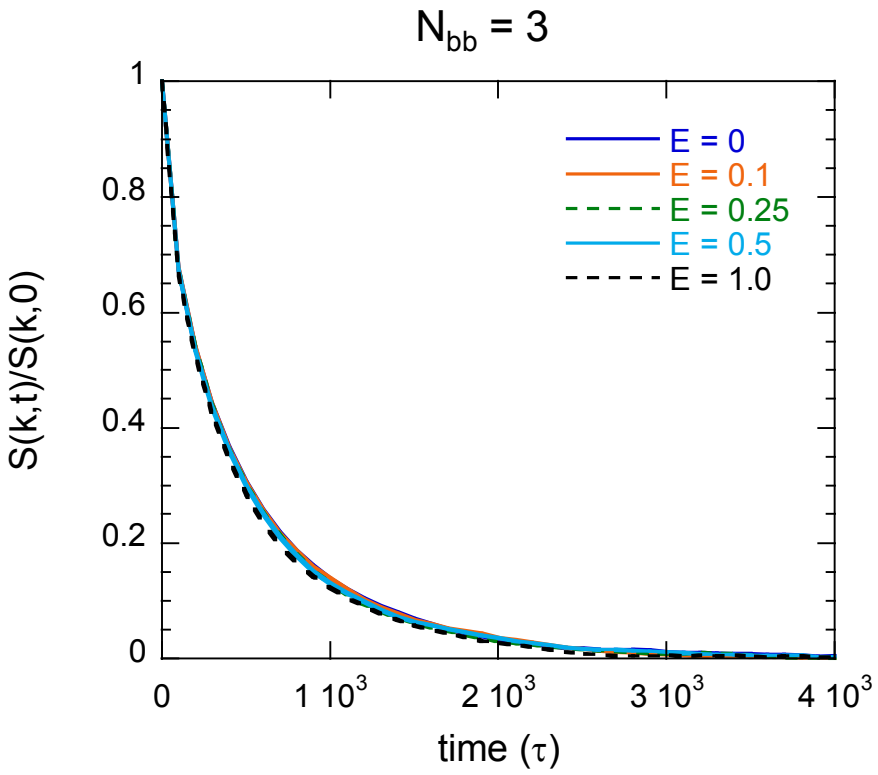
if ions are uncorrelated: $\lambda^{NE} = \frac{e^2\rho}{kT}(D_+ + D_-)$

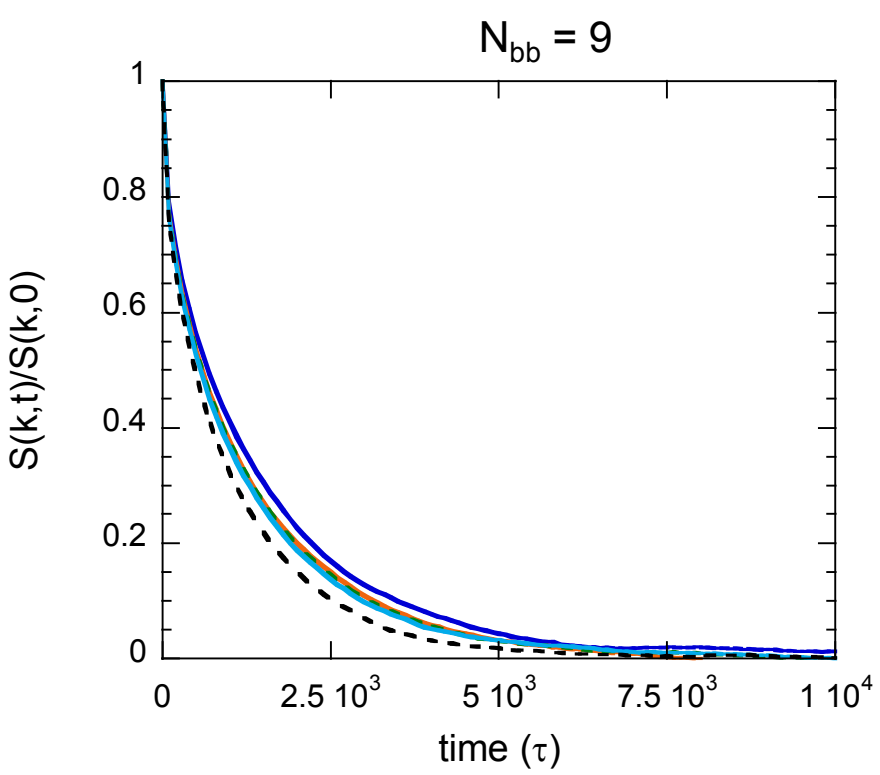
system	λ	λ^{NE}	$\alpha = \lambda/\lambda^{NE}$
ionene N = 3	5.7×10^{-4}	1.6×10^{-3}	0.36
ionene N = 9	2.4×10^{-5}	1.3×10^{-4}	0.18
pendant N = 3	2.7×10^{-4}	7.5×10^{-4}	0.36

Time-Dependent Structure Factors

ionenes

decay at the ionomer peak

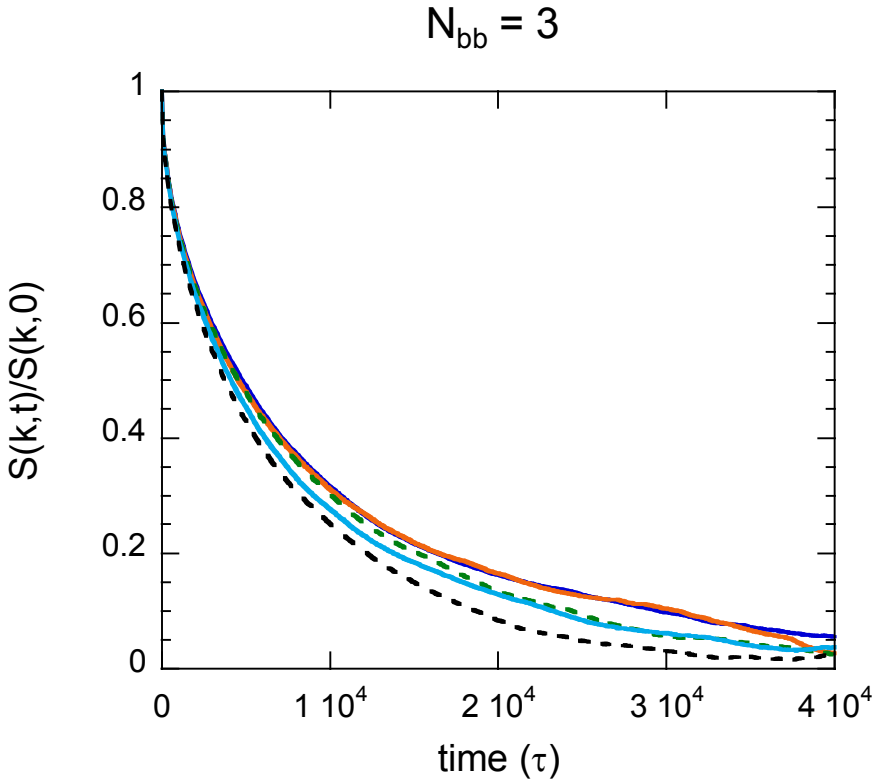


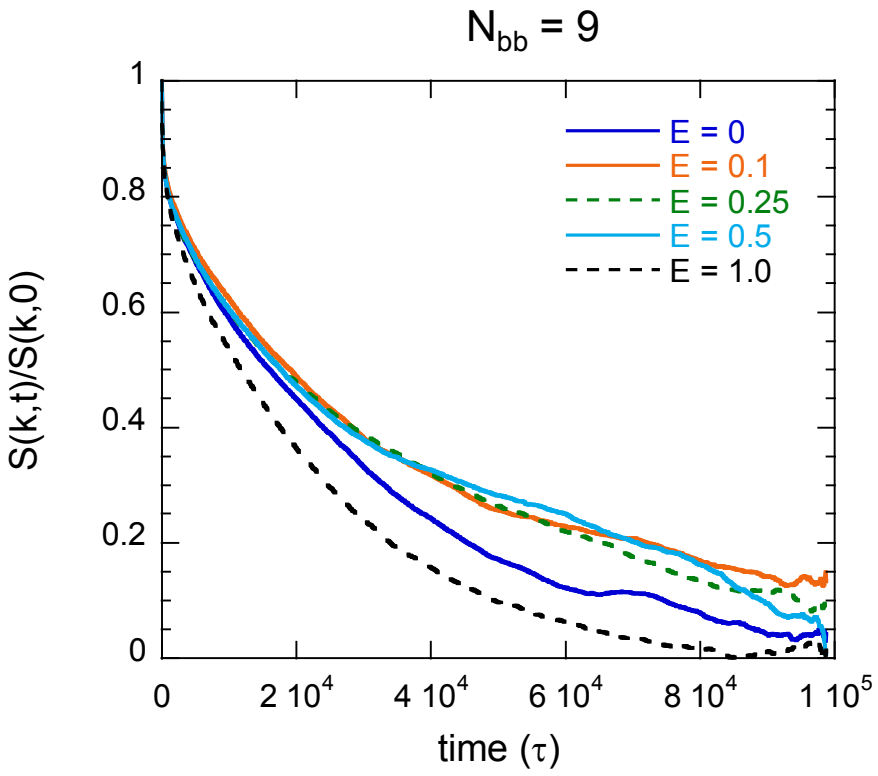


field speeds up decorrelation of clusters

Time-Dependent Structure Factors

pendants





field slows down motion!
why?

The New Picture

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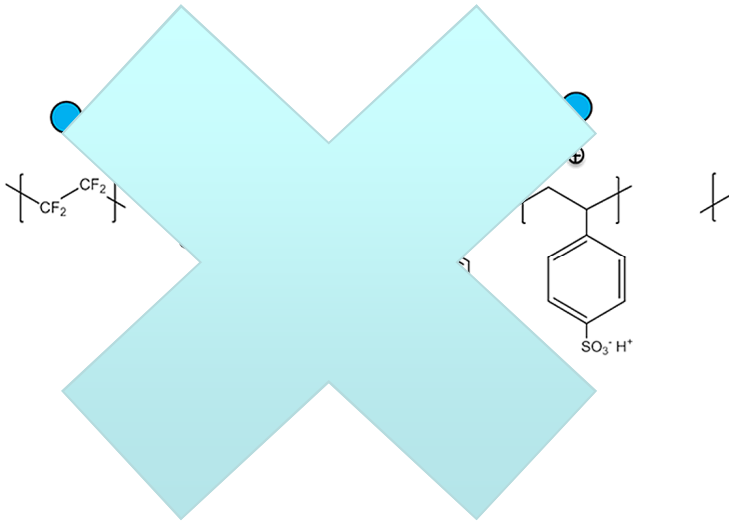
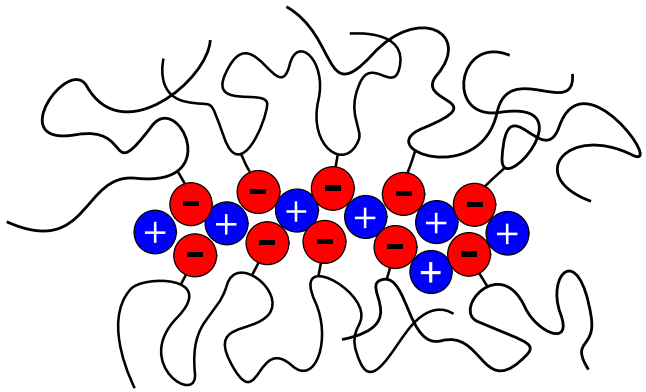
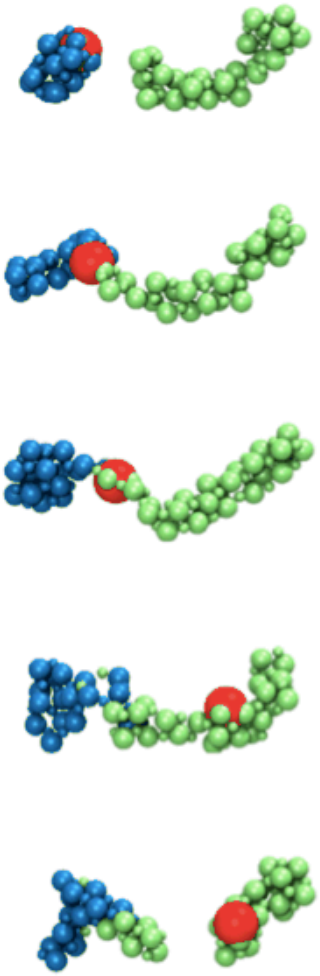
stringy morphologies





ion motion by cluster rearrangment



Conclusions

- aggregates have many shapes
- molecular architecture important
  - isolated aggregates for pendants or large spacing
  - percolation for ionenes or short spacing
- ion motion by cluster rearrangment
- ions diffuse faster in percolated morphologies
- ion motion is correlated

coarse-grained

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

atomistic

Alam et al., *Materials* **5**, 1508 (2012)
Bolintineanu et al., *ACS Macro Lett.* **2**, 206 (2013);
Bolintineanu et al., *Macromolecules* **46**, 5381 (2013);
Lueth et al., *J Chem Phys* **140**, 054902 (2014)

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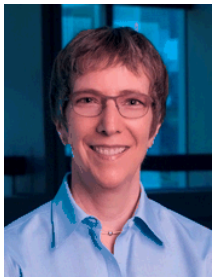

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University of Pennsylvania

Jim Runt, Penn State

The "Ionomers" LDRD team
Funding: Sandia LDRD Program
CINT
NERSC

Average Local Structure

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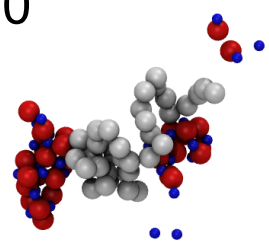
one polymer (white, red anions) and nearby ions (red anions, blue counterions)
N_{bb}=9, frames are 1000 steps apart

periodic pendant, frames averaged:

0



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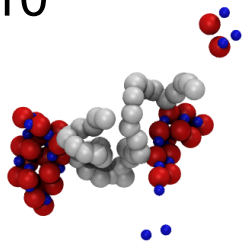

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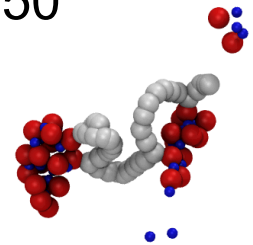

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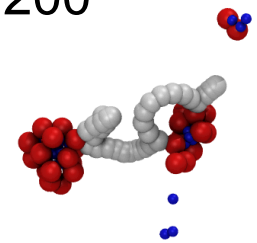

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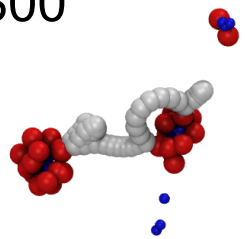
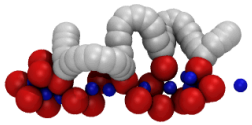
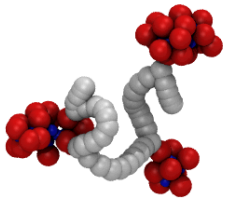


other periodic pendant examples

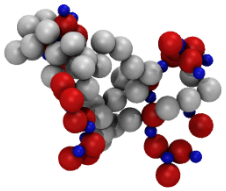
200





periodic ionene, frames averaged:

0



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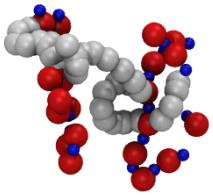

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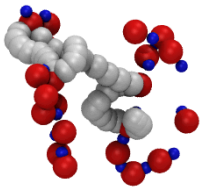

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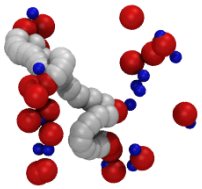

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