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Nonequilibrium Simulations of Ion Dynamics in Ionomer Melts

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Sandia National Laboratories

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Exceptional service in the national interest

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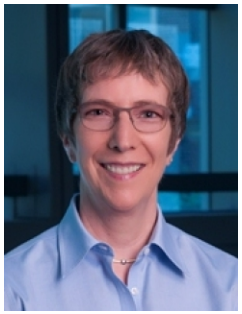

Karen Winey
U Penn

Jim Runt
Penn State

The “Ionomers” LDRD team
Funding: Sandia LDRD Program
CINT

Ionomers as Single-Ion Conductors

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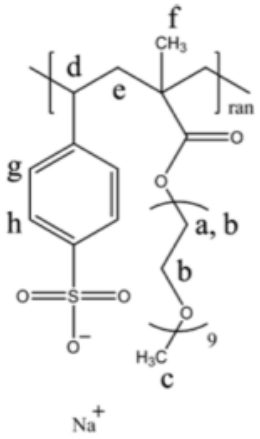
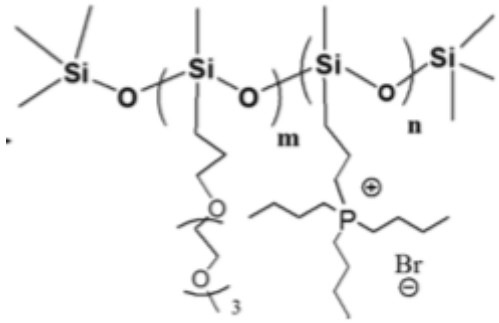
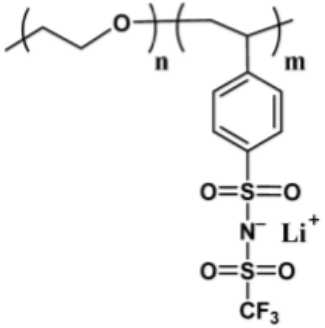
(no solvent)

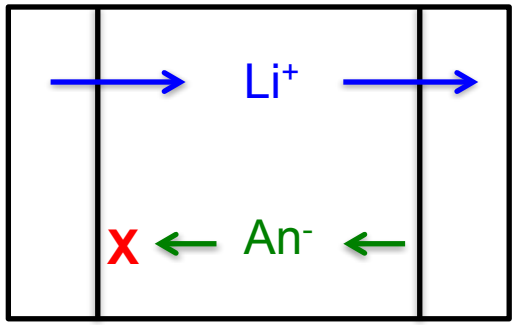






why single-ion?

- high transference number
- no concentration gradients



Wang, J.-H. H. *et al. Macromolecules* **48,** 7273–7285 (2015).
Liang, S. *et al. Macromolecules* **47,** 4428–4437 (2014).
Rojas, A. A. *et al. Macromolecules* **48,** 6589–6595 (2015).

Ionic Aggregates in Ionomers

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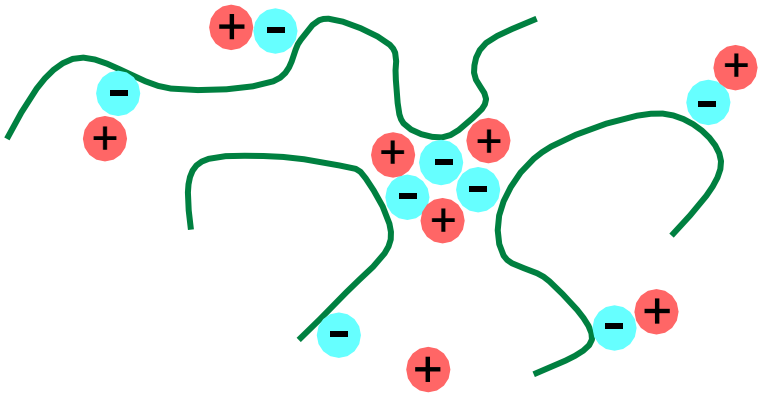
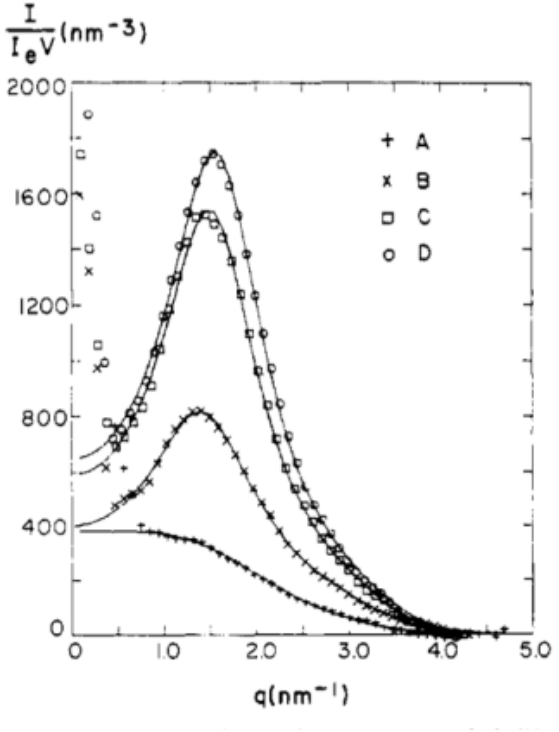
Coulombic forces favor aggregates
polymer entropy limits size



nm-scale ionic aggregates

"ionomer peak"

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



Yarusso & Cooper, Macromolecules, 1983

Ionic Conductivity in Ionomers

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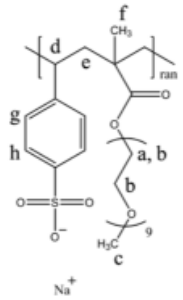
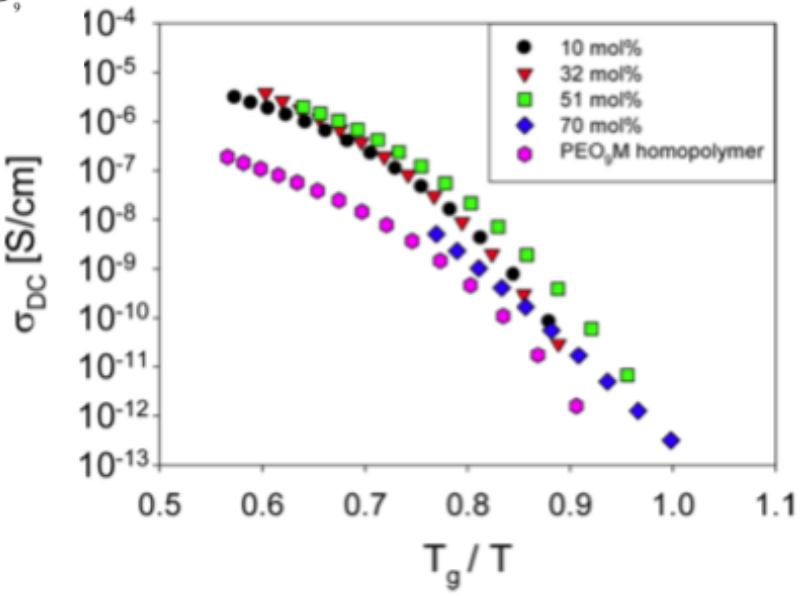
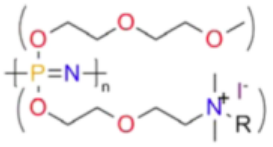
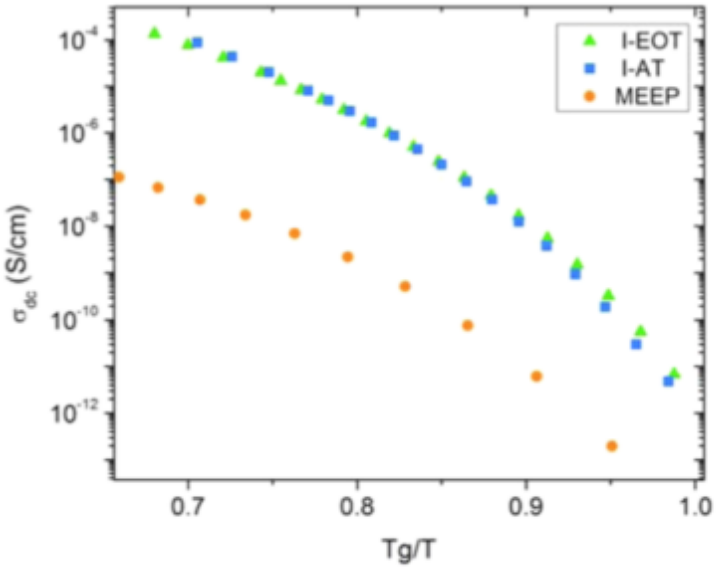
low due to low ε, slow polymer motion, ionic aggregates





Wang, J.-H. H. *et al. Macromolecules* **48,** 7273–7285 (2015)



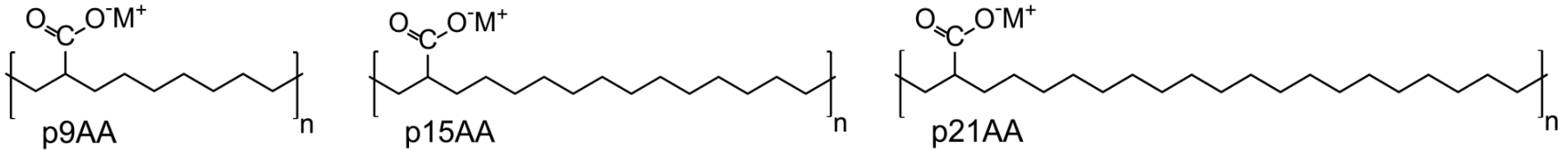


Bartels, J. *et al. Macromolecules* **48,** 111–118 (2015)

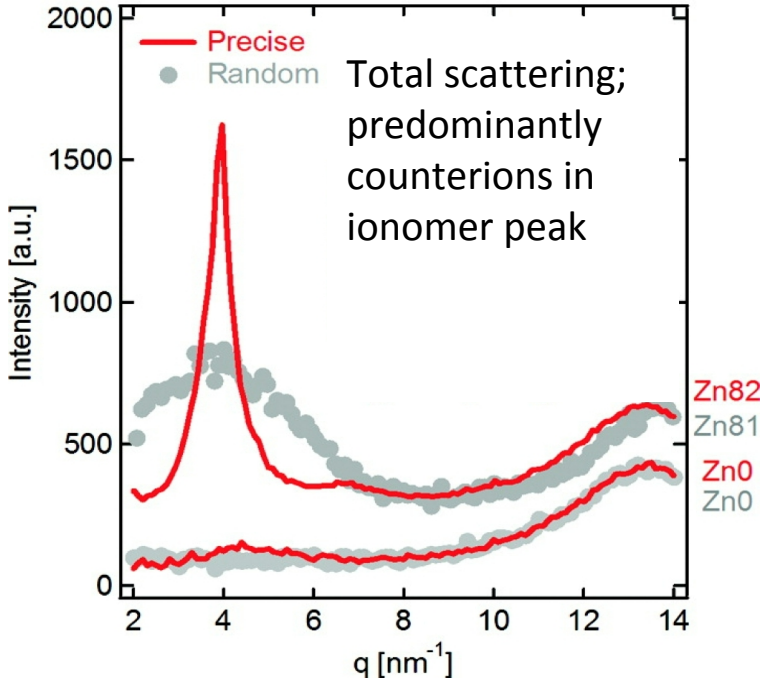
need $\sigma_{DC} > 10^{-3}$ S/cm for applications

A Model System: Precise Ionomers

PE backbone with **precisely** spaced carboxylic acid functional groups



Wagener group, University of Florida



M. E. Seitz et al., *J. Am. Chem. Soc.* **2010,** 132, 8165-8174.

Atomistic Simulations

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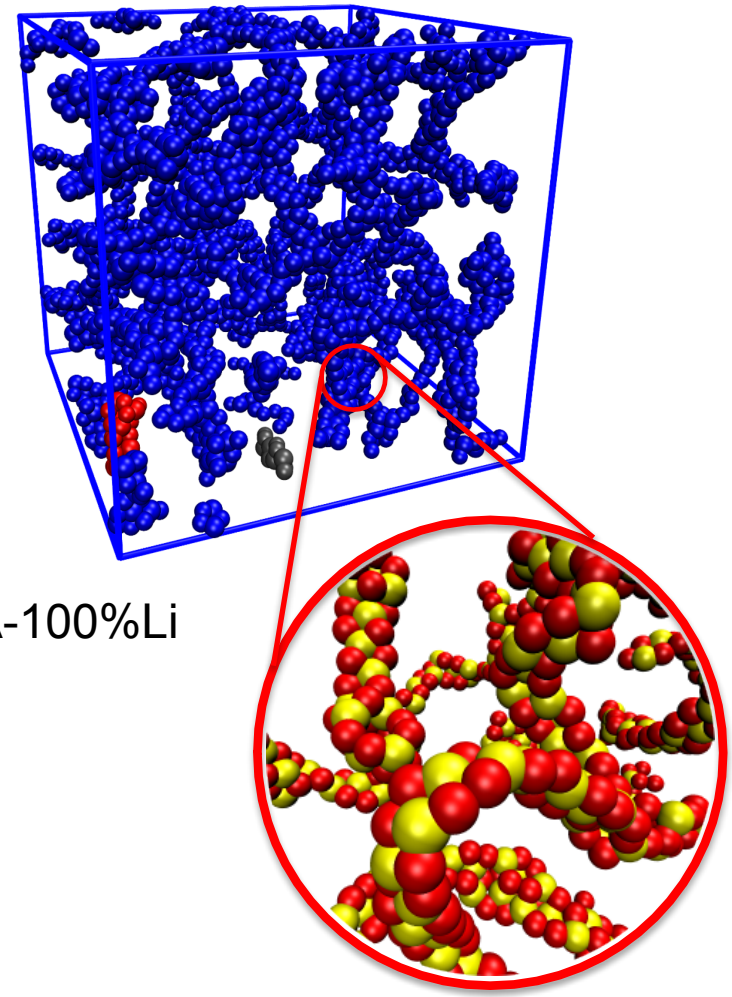
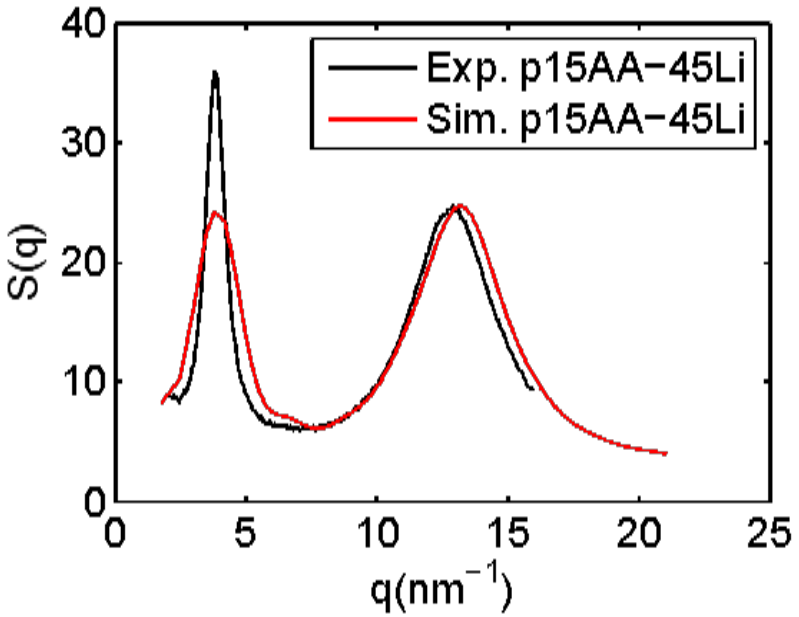
often see stringy aggregate morphologies



p9AA-100%Li

scattering matches exp.



Bolintineanu et al., *ACS Macro Lett.* **2**, 206 (2013)
Buitrago et al, *Macromolecules* 48, 1210 (2015)

Coarse-Grained Simulations

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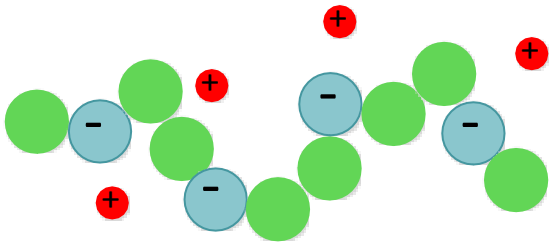
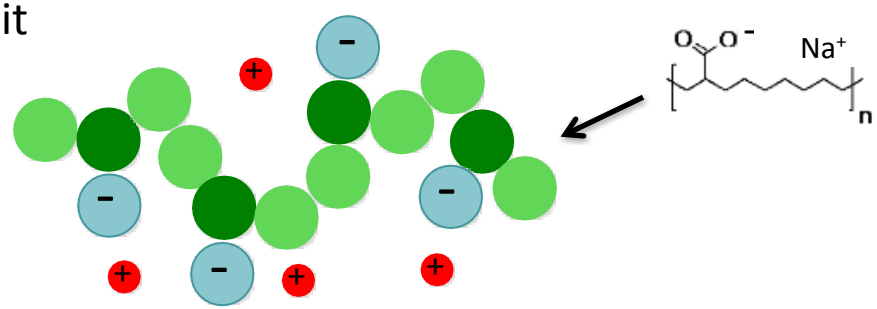
Ions in the polymer backbone:
"**ionenes**"



backbone beads per repeat unit

N = 3

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



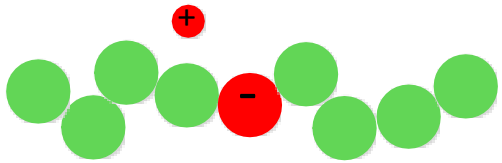
N = 3, 5, 7, 9 (11)
35 or 36 backbone beads
800 polymers
counterion size = 0.5 σ

bulk dielectric constant = 4
Bjerrum length = 35.7σ
when Coulomb energy = kT

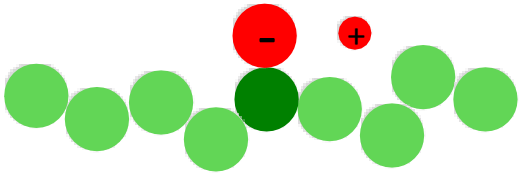
$$\ell_B = \frac{e^2}{4\pi\varepsilon_0\varepsilon_r kT} = 35.7\sigma$$

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

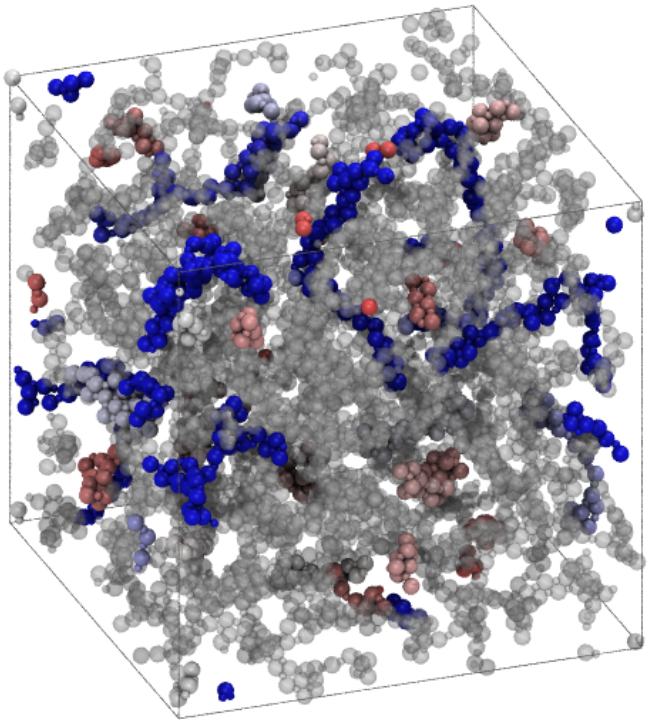
CG Simulations: Architecture Matters



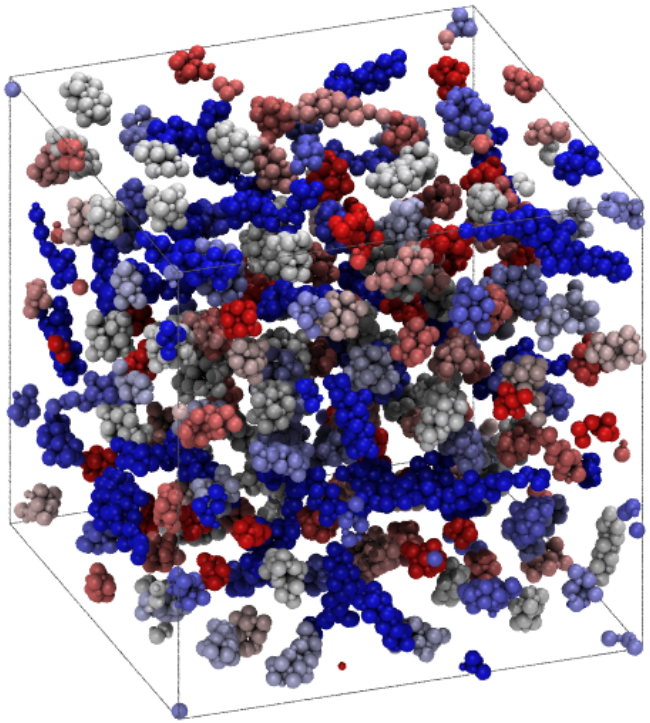
Ionenes: percolated



Pendants: not percolated



N = 9



Small clusters → Large clusters

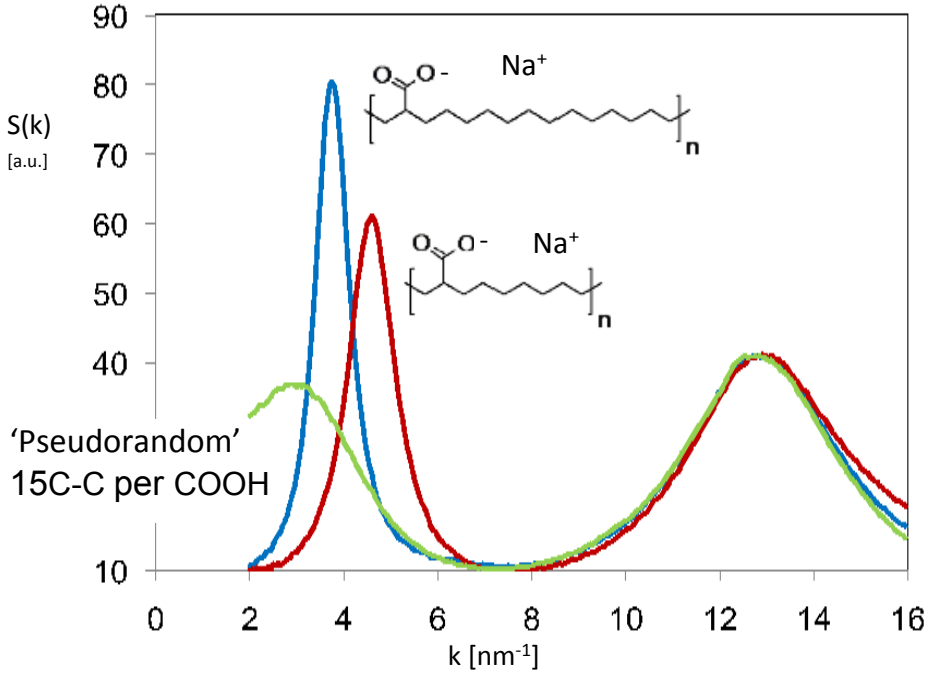
Only charged beads shown

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

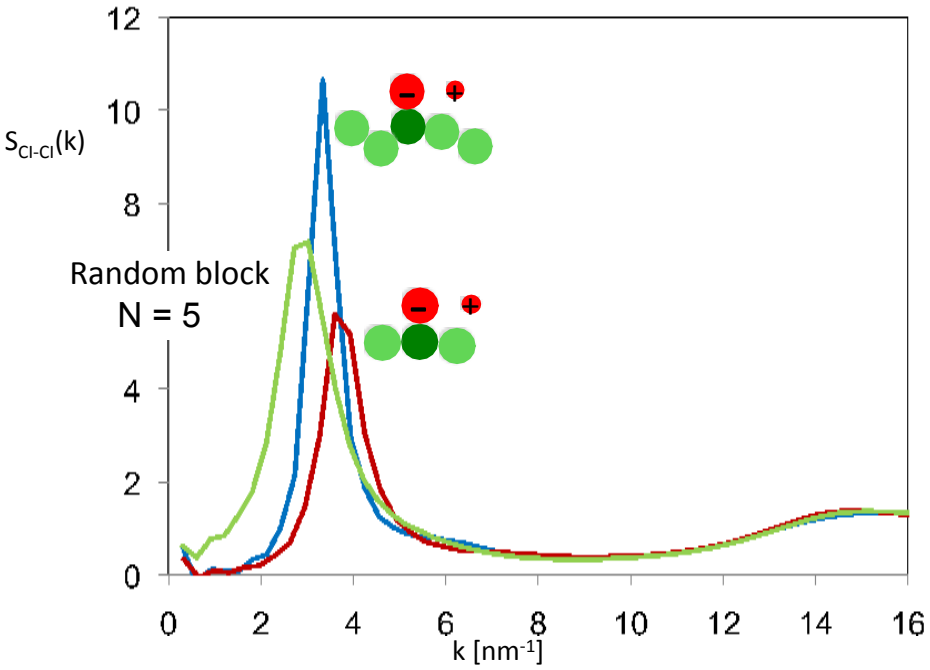
CG MD: Comparison to X-ray Scattering

- Experimental/simulation agreement for pendants
  - 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)

Movies

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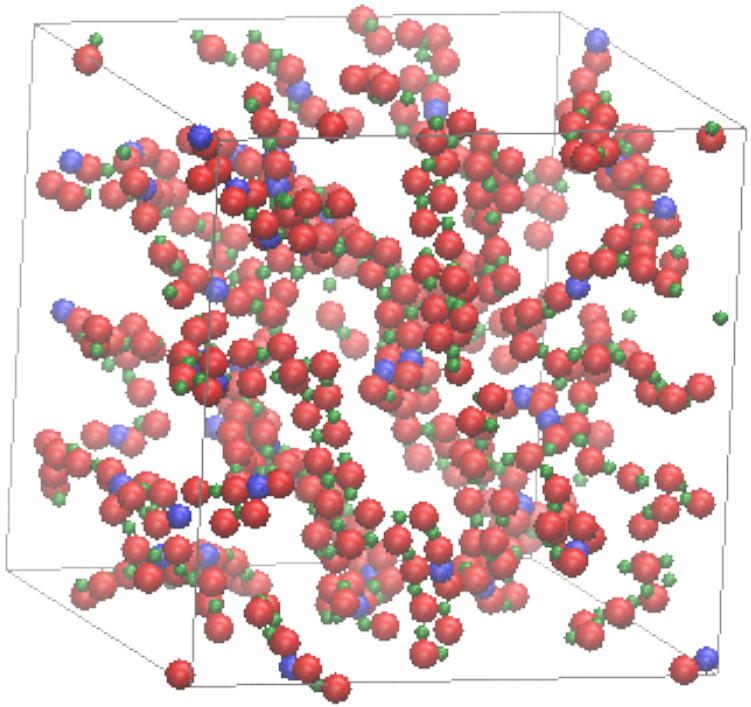
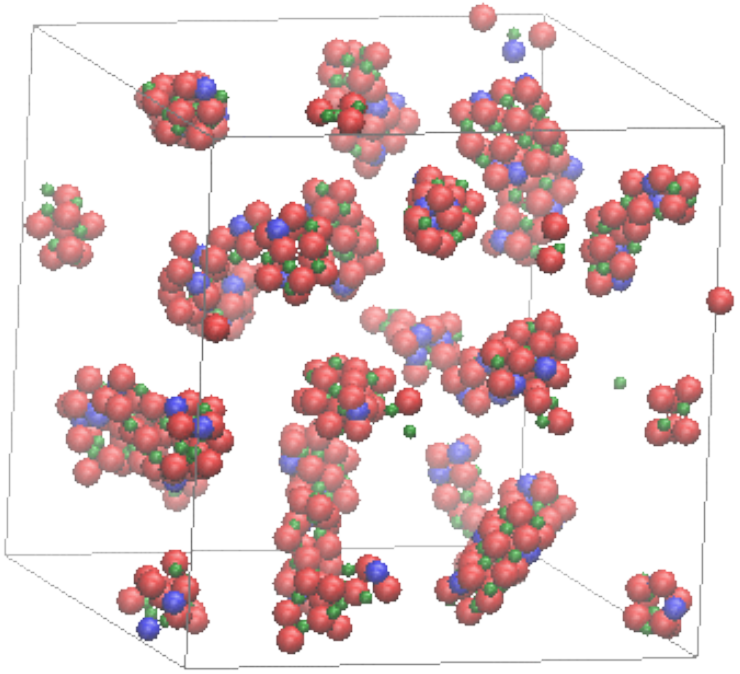
ionenes N = 9



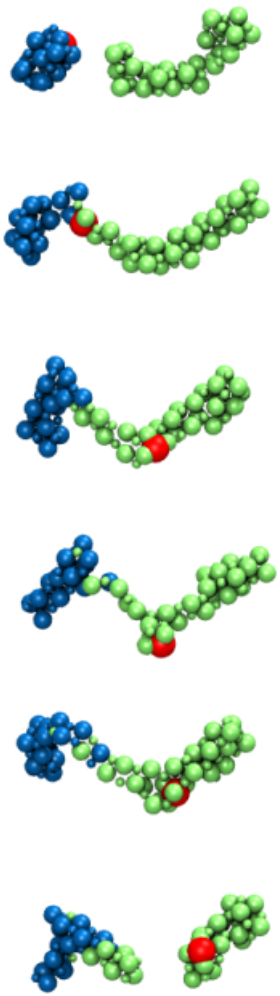
pendants N = 9



Ion Trajectories

periodic pendants N = 9

2 separate clusters
Follow one cation



time

Clusters have collided

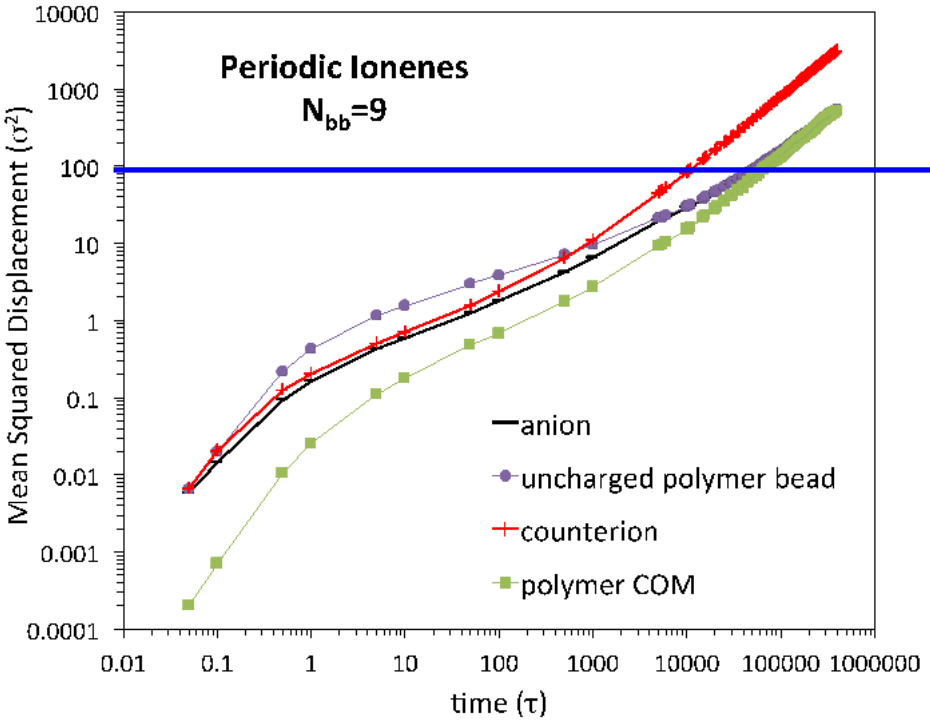
Ion has moved to other cluster.
NEVER separated from a cluster.

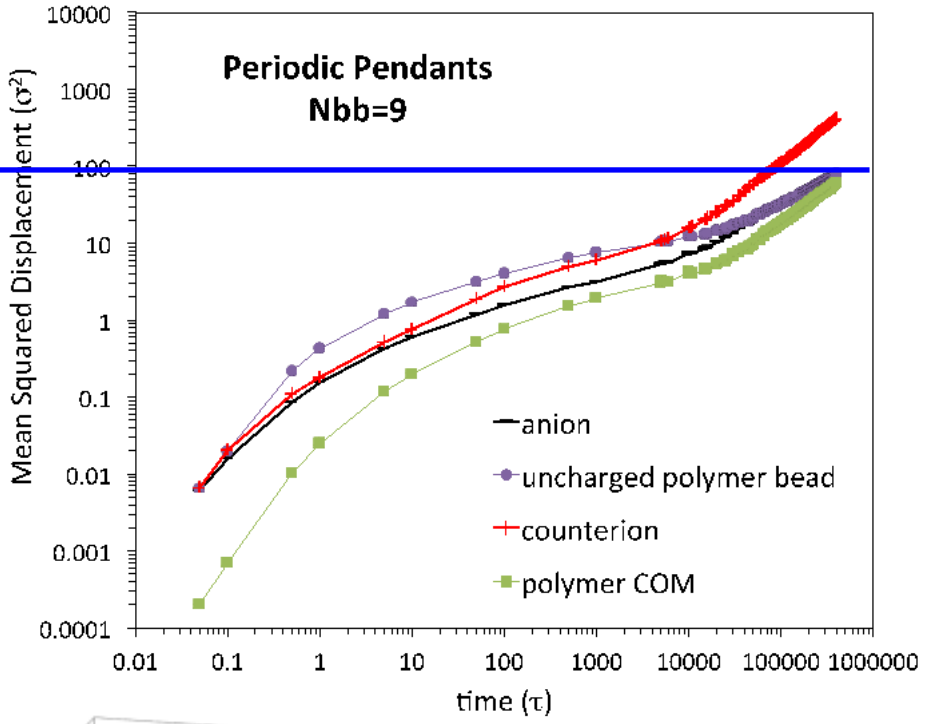
Clusters reform with ion moved

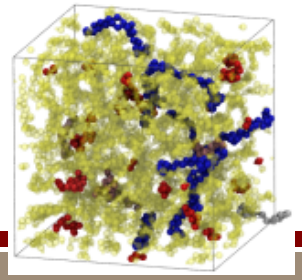
ions move by cluster rearrangment/collision

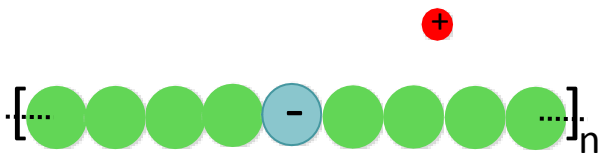
Mean Squared Displacements

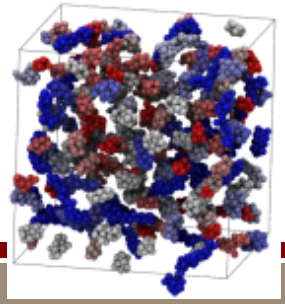
- Ionenes, pendants similar at short times
- Pendants slower but qualitatively similar at long times

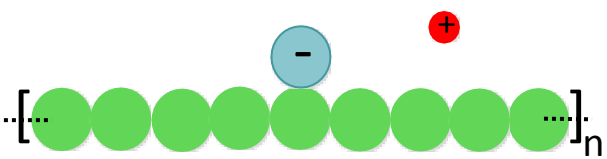










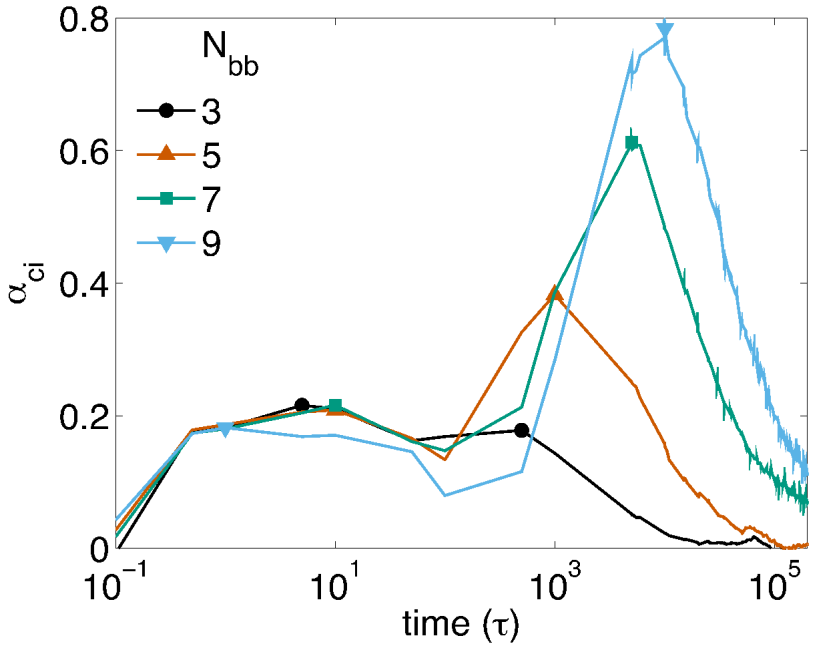


Ion Dynamics

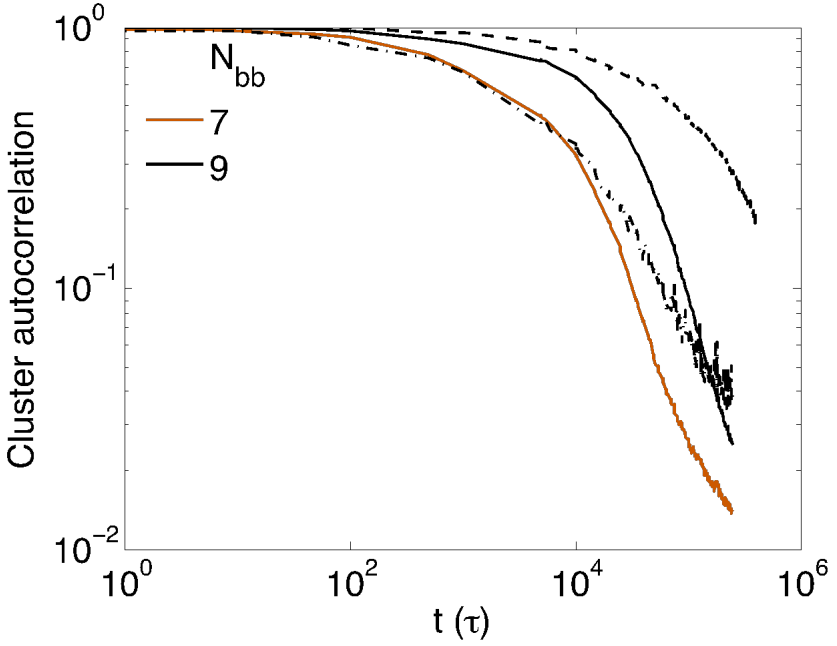
non-Gaussian parameter

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

cations in periodic pendants



ion cluster auto-correlation



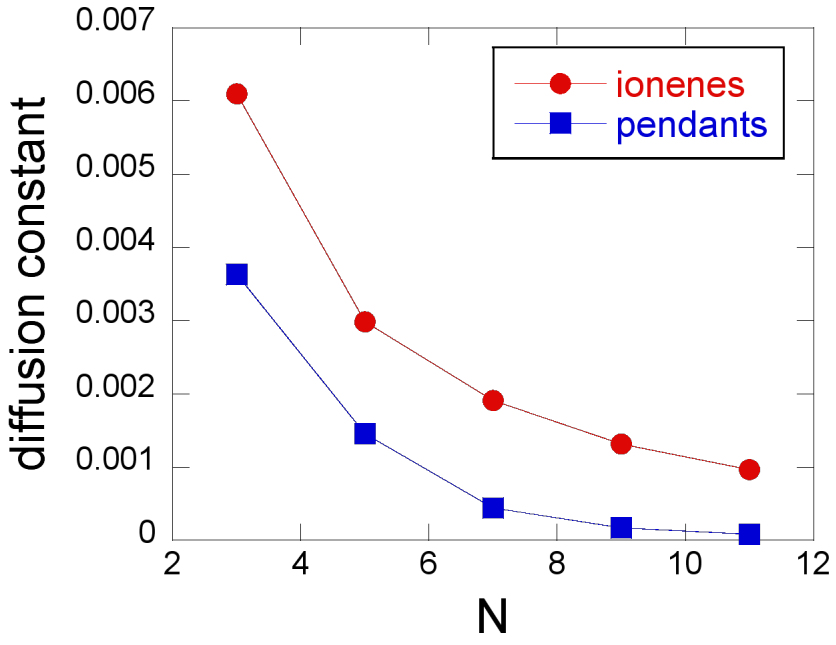
indicative of 2 time scales:

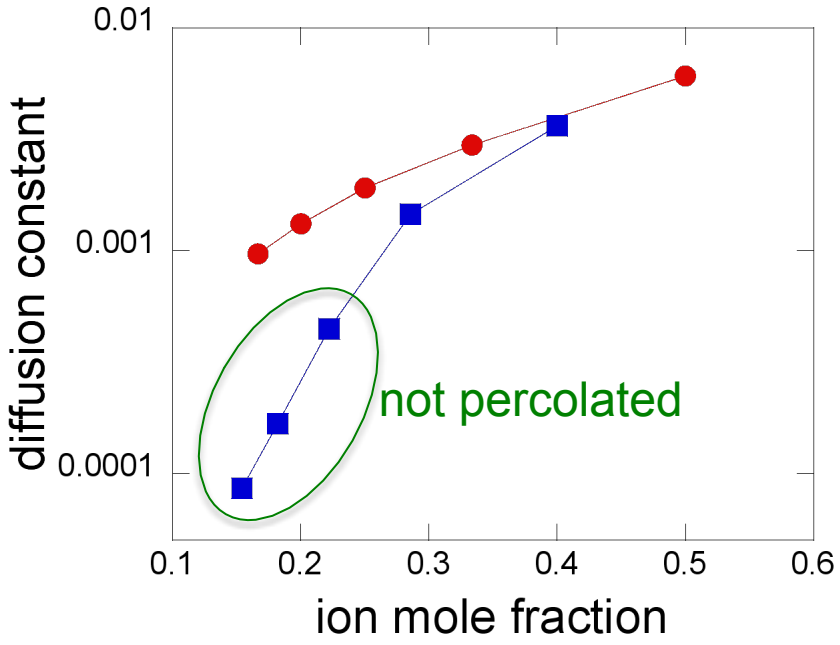
- local motion in clusters
- slower rearrangement between clusters

p7: τ_c = 8000 τ
p9: τ_c = 31000 τ

Counterion Diffusion Constants

$$\langle \mathbf{r}^2(t) \rangle = 6Dt$$





- Ionenes have faster diffusion than pendants
- Percolated systems have faster diffusion

Hall et al., *Macromolecules* (2012)

Effect of Field: Ionenes

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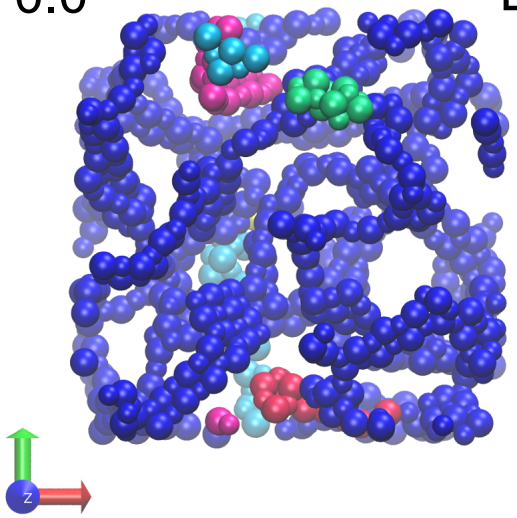
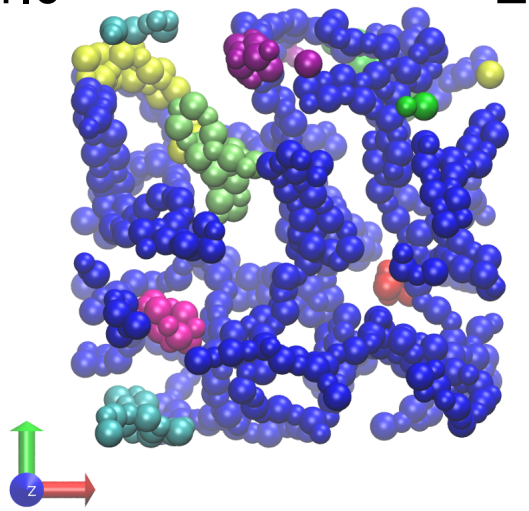
add force $F_x = qE_x$ to each ion

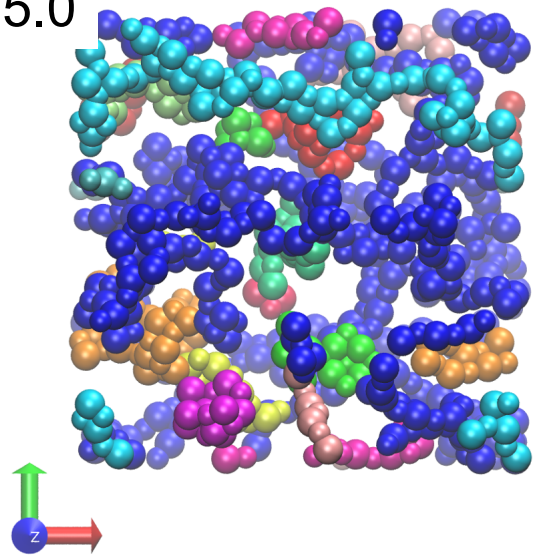
E = 0.0



E = 1.0



E = 5.0



field direction

Effect of Field: Pendants

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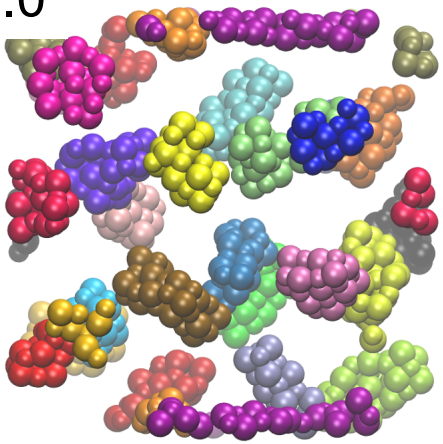
E = 0.0



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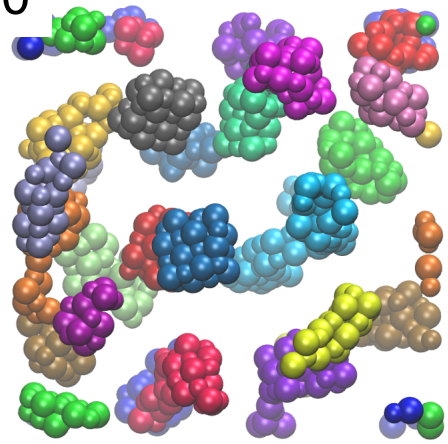

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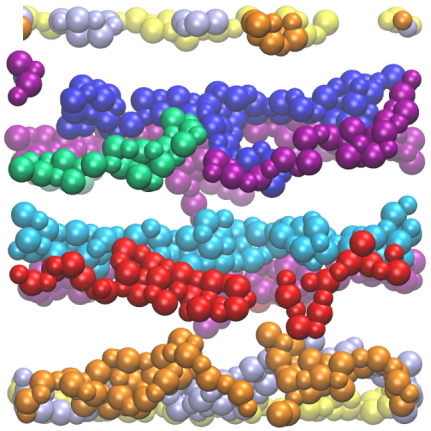

field direction

MSDs in the Field

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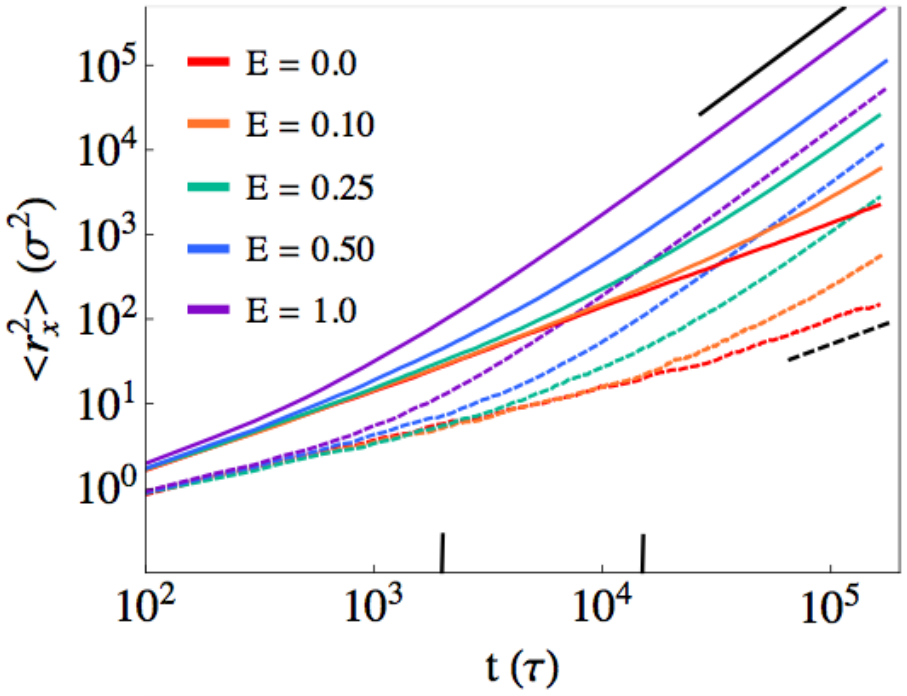
diffusion

$$\langle r_x^2 \rangle \sim Dt$$

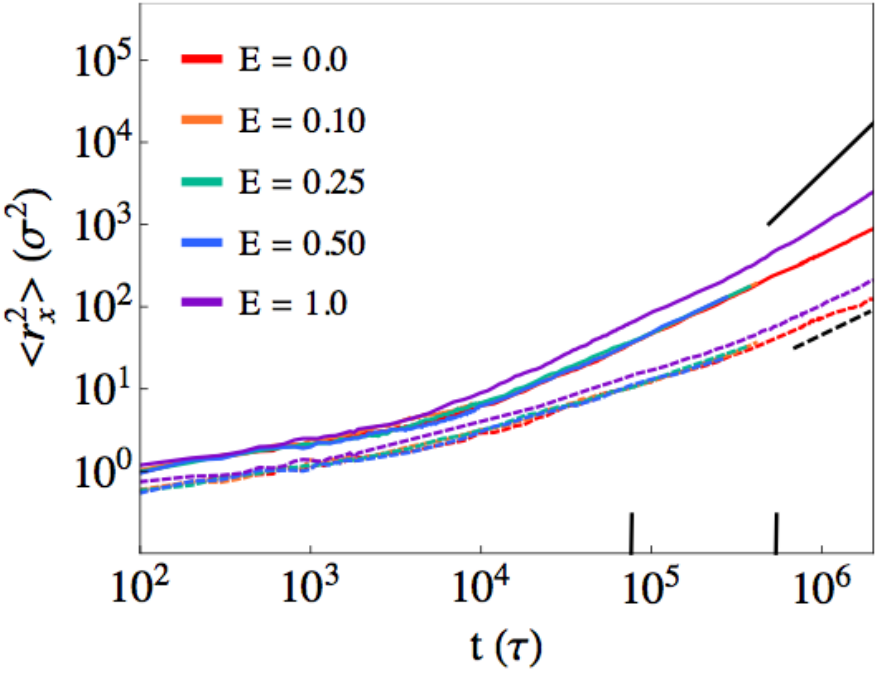
drift in the E field

$$\langle r_x(t)^2 \rangle_E - \langle r_x(t)^2 \rangle_0 = \langle v_x^2 \rangle t^2$$

ionene N = 3



pendant N = 9



dashed = anion, solid = cation

Time-dependent Structure Factors

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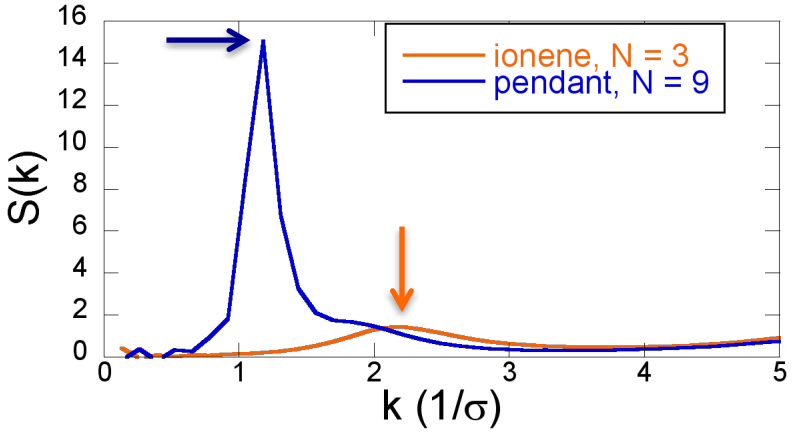
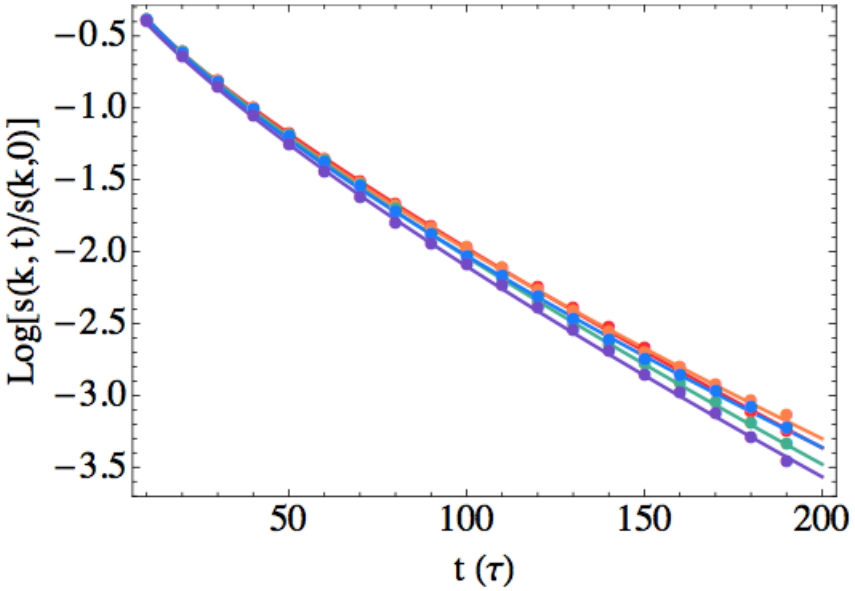
decay of counterion-counterion scattering peak

$$S(k,t)/S(k,0) = \exp[(-t/\tau)^{\beta}]$$

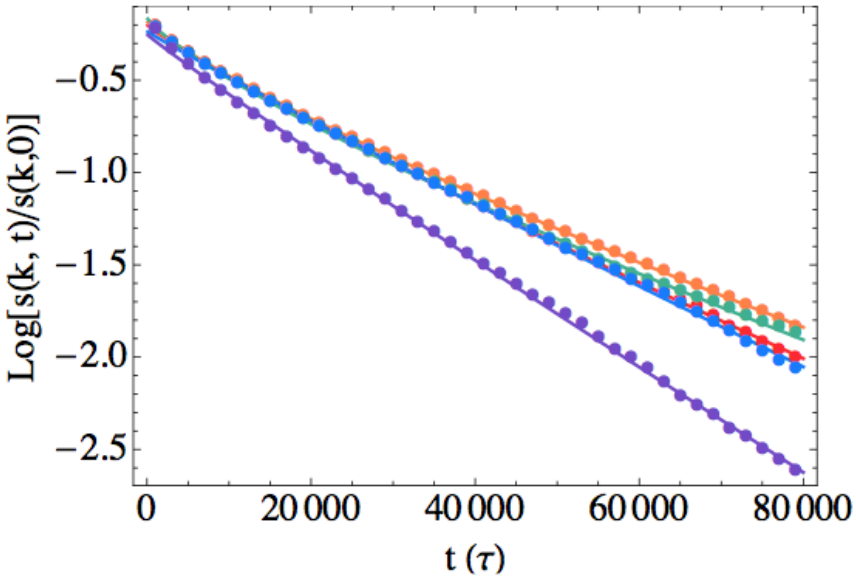
$0.66 < \beta < 0.96$



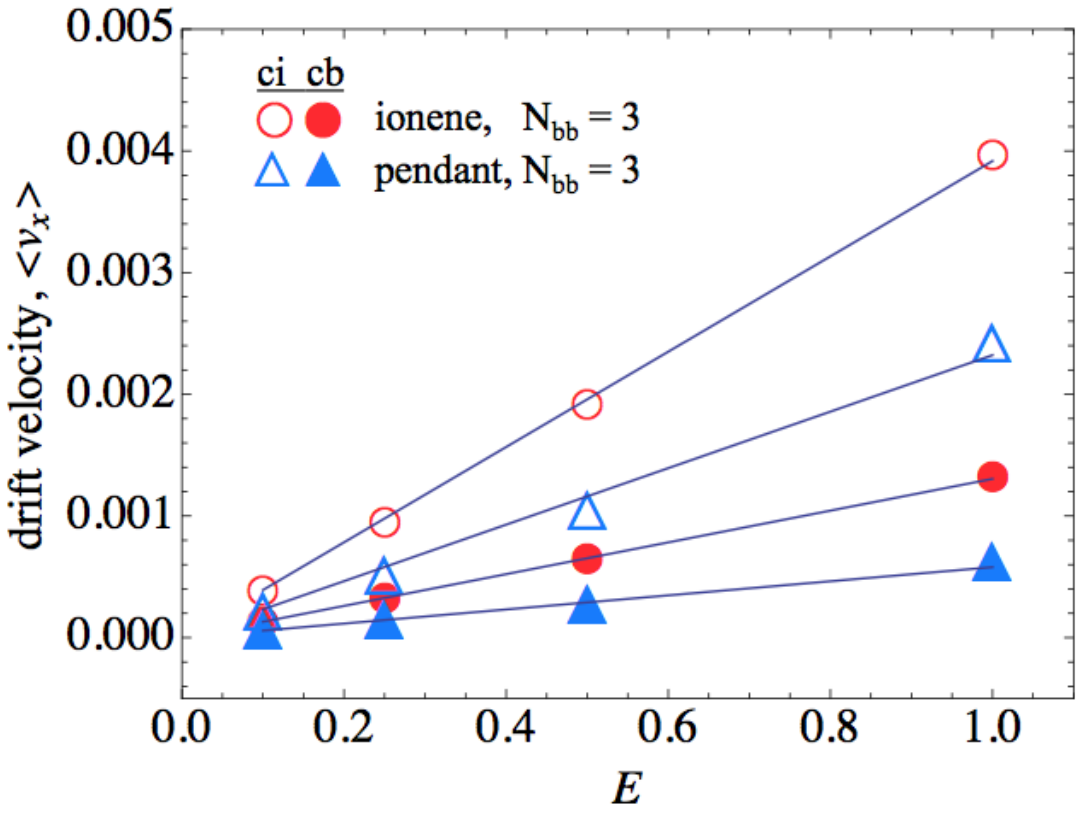
ionenes N = 3



pendants N = 9



Drift Velocity

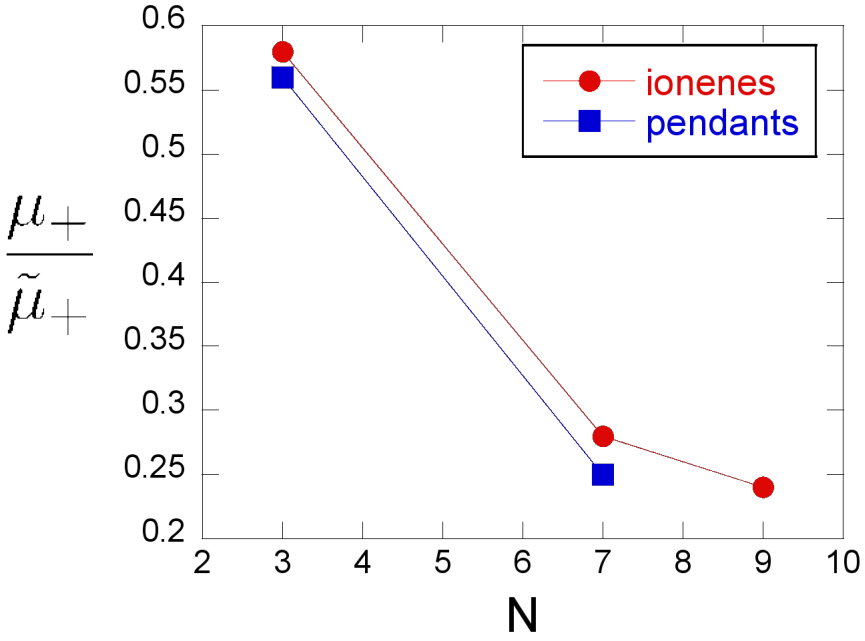


in linear response regime
polymers are short so they also move

Ion Mobilities

from non-equilibrium simulation in field: $\mu_i = \langle v_{x,i} \rangle / E$

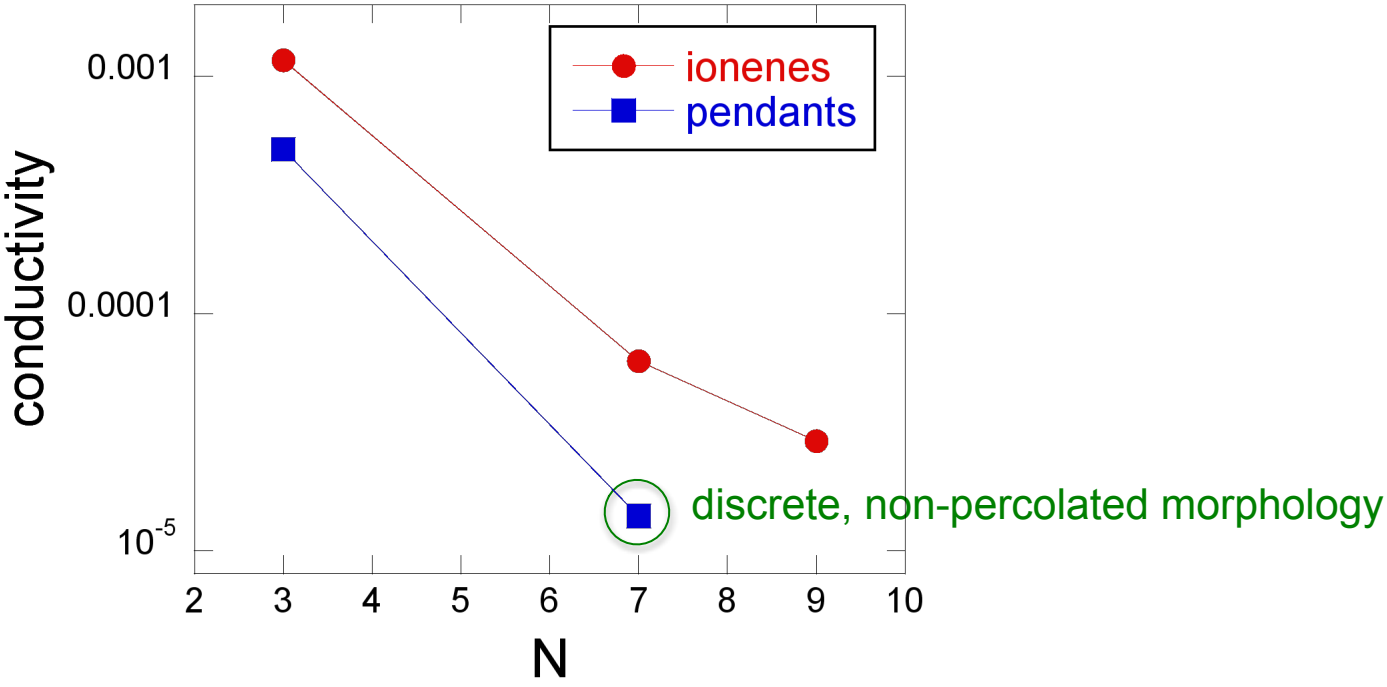
from equilibrium Einstein relation $\tilde{\mu}_i = zeD_i/kT$



ion motion is correlated

Conductivity

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

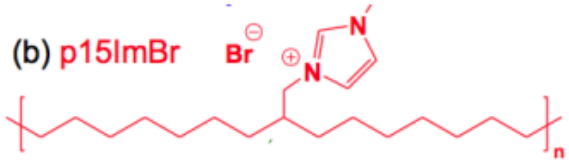


- conductivity decreases with decreasing ion concentration
- lowest for non-percolated aggregate morphology

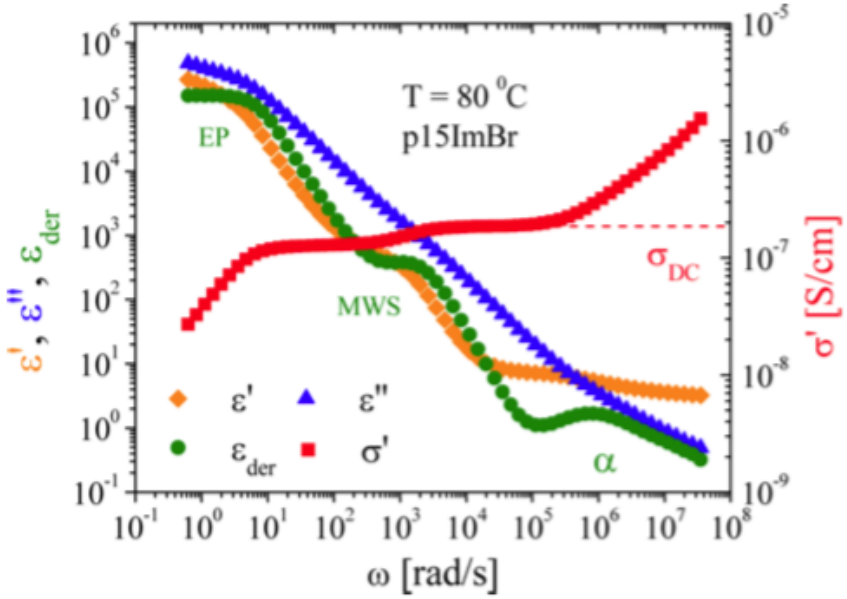
Ting et al., *Macromolecules*, 2015

Oscillating fields

Why? would like to understand DRS experiments



$$\epsilon_{der} = -\frac{\pi}{2}\frac{\partial \epsilon'(\omega)}{\partial \ln \omega}$$



- how many free ions? ion pairs? aggregates?
- what molecular motions lead to the α relaxation?
- how is the MWS relaxation related to the aggregate morphology?

Choi, U. H. *et al. Macromolecules* **48,** 410–420 (2015)

Oscillating Electric Fields

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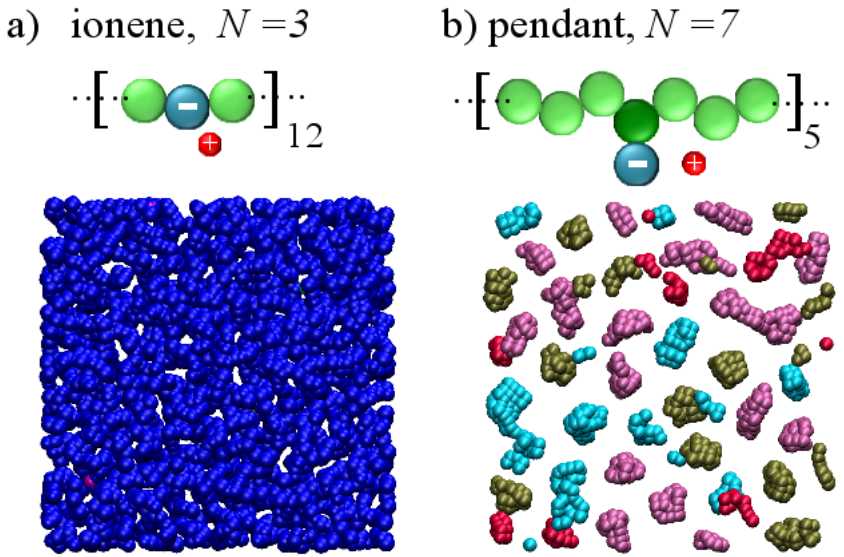
systems simulated

- a fast, percolated system: ionenes with N = 3, “i3”
- a isolated cluster system: pendants with N = 7, “p7”
- polymers have 36 (i3) and 35 (p7) backbone beads
- also simulate 1 repeat unit of each, the “monomers”



apply field in x direction

$$E_x = E_0 \sin \omega t = \mathrm{Re}\left(E_0 i e^{-i\omega t}\right)$$

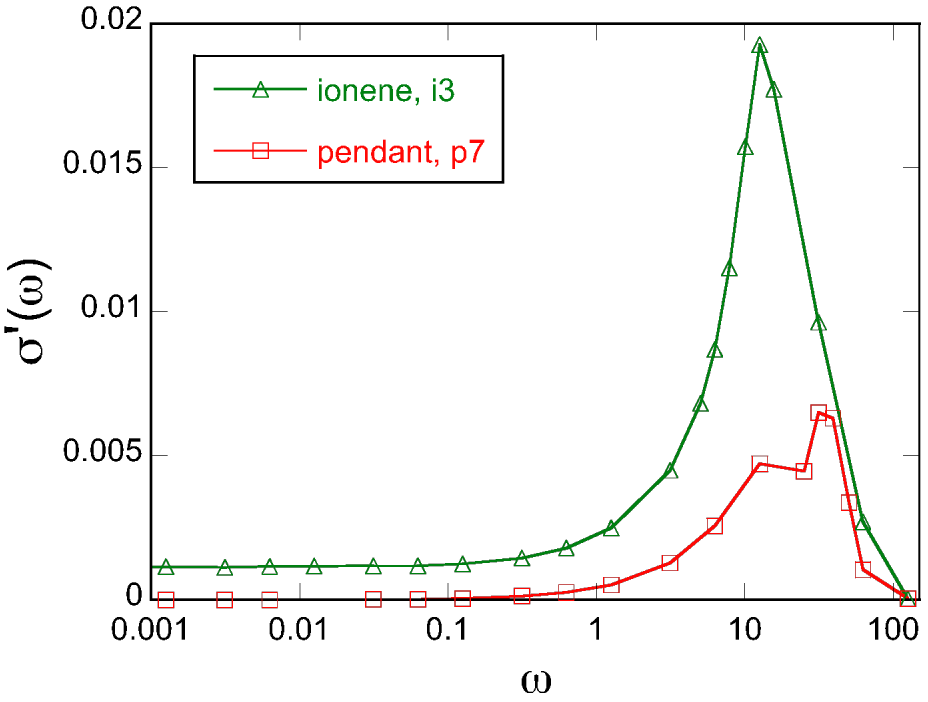
$E_0 = 1$ is in linear response regime

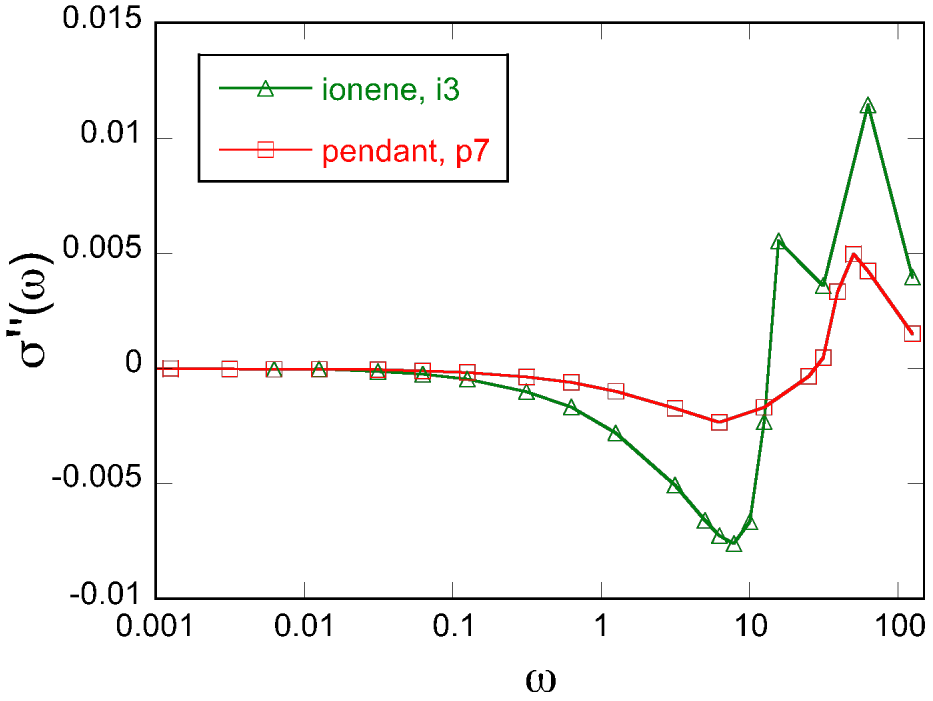
Frequency-dependent σ(ω)

Sandia National Laboratories

apply field $E_x = E_0 \sin \omega t = \mathrm{Re}\left(E_0 i e^{-i\omega t}\right)$

calculate current $j_x(\omega, t) = \frac{e}{V} \sum_i z_i v_{x,i} = \sigma(\omega) E_x(\omega, t)$





Frequency-dependent σ(ω)

Sandia National Laboratories

apply field $E_x = E_0 \sin \omega t = \mathrm{Re}\left(E_0 i e^{-i\omega t}\right)$

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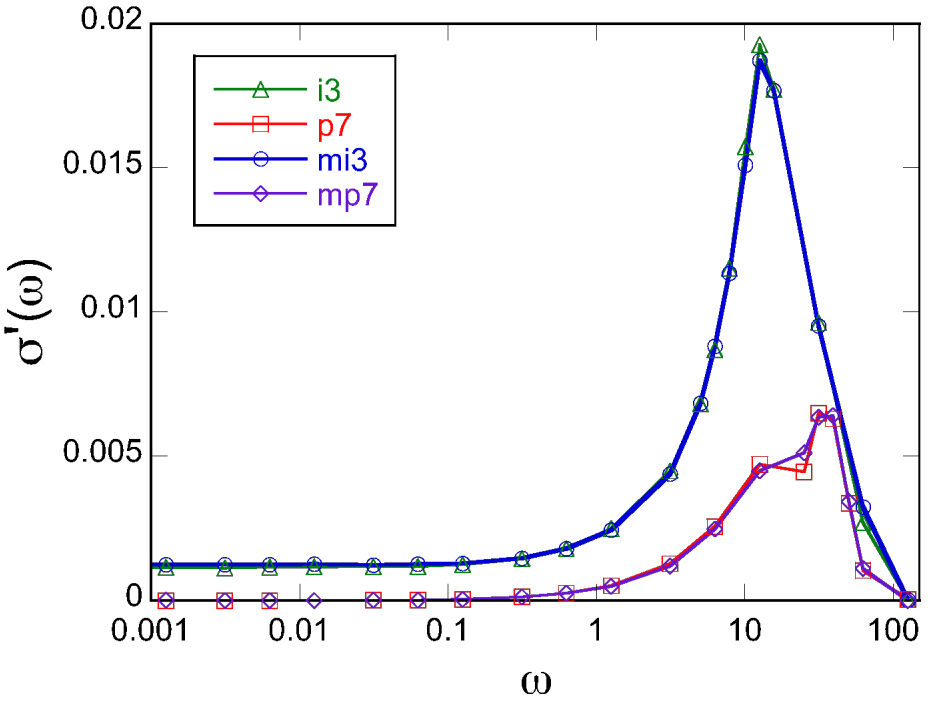
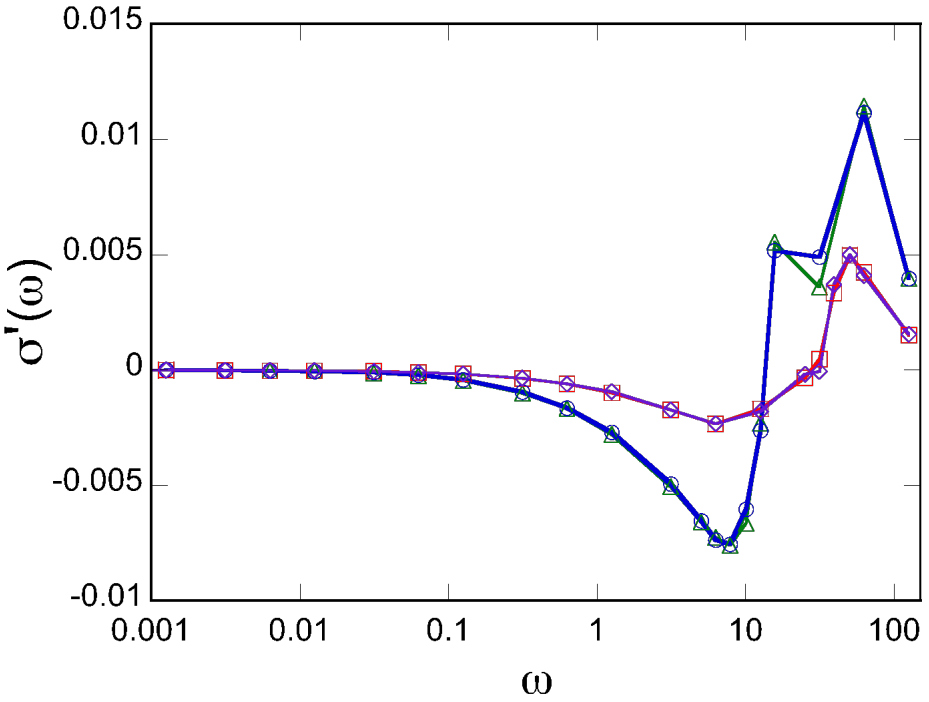
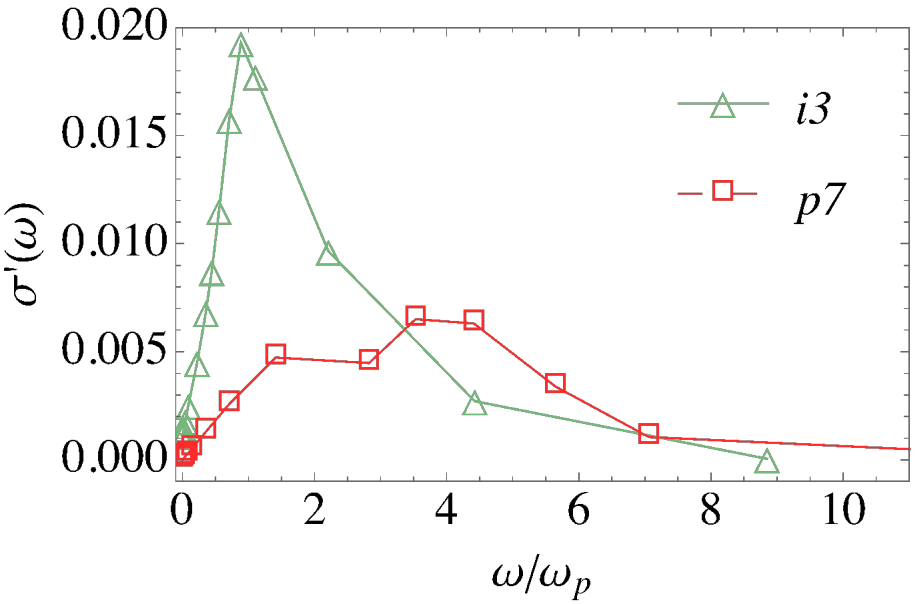


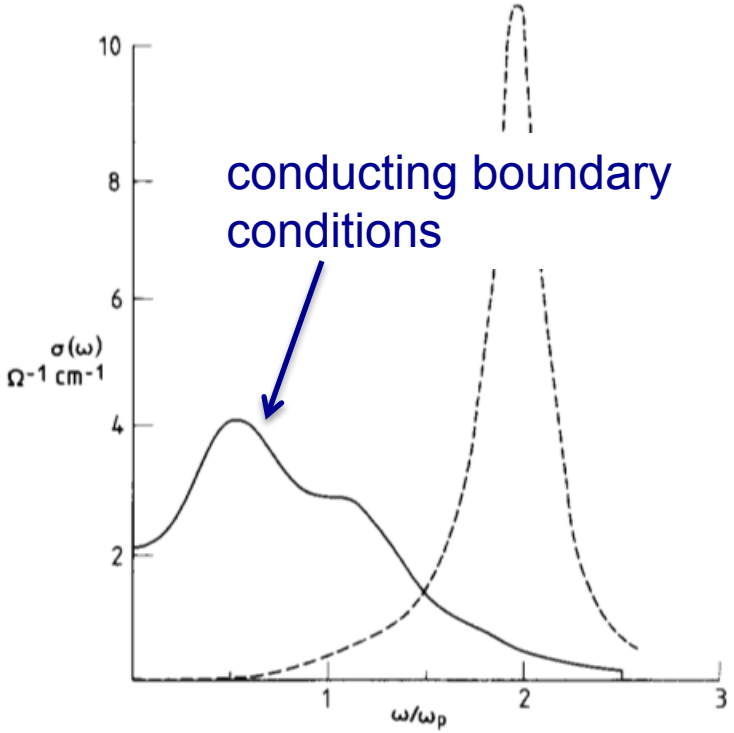


Plasma Oscillations

peak near plasma frequency ω_p



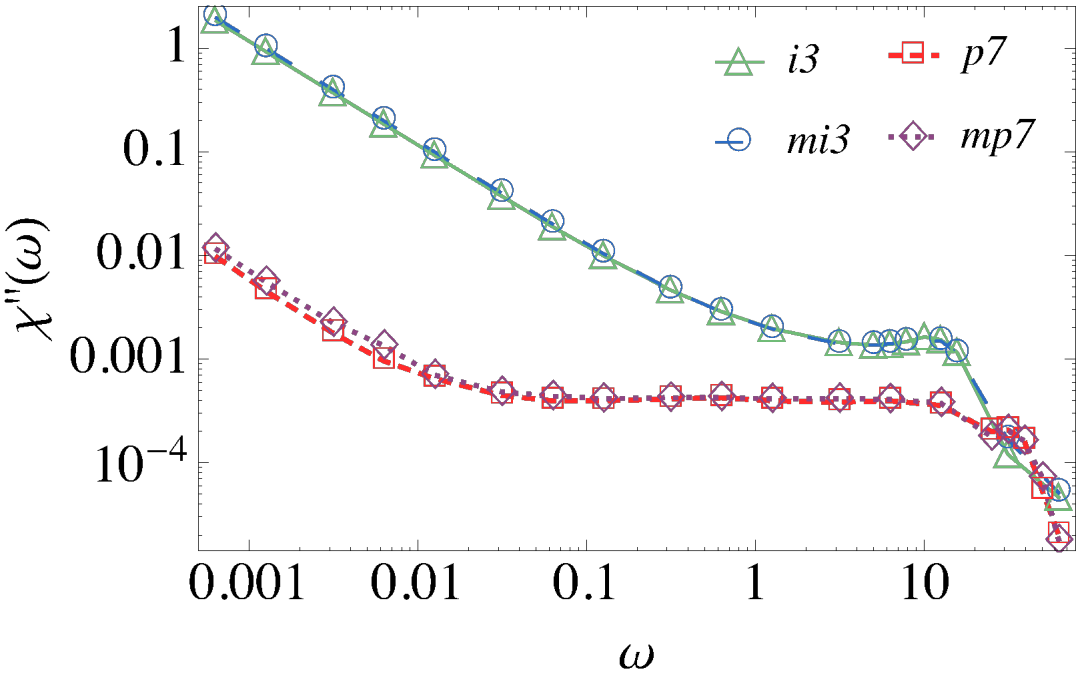
MD simulations of molten salt



De Leeuw, S. W. & Perram, J. W. *Physica A* 107A, 179 (1981)

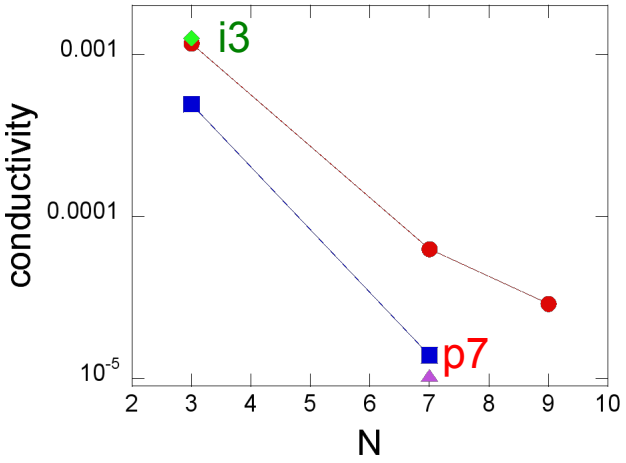
Lower Frequencies

$$P_x(\omega,t) = \frac{e}{V}\sum_i z_i r_{x,i} = \chi(\omega)E_x(\omega,t)$$



$$\sigma(\omega) = -i\omega\chi(\omega)$$

$$\sigma'(0) = \lim_{\omega\to 0}(\omega\chi''(\omega))$$

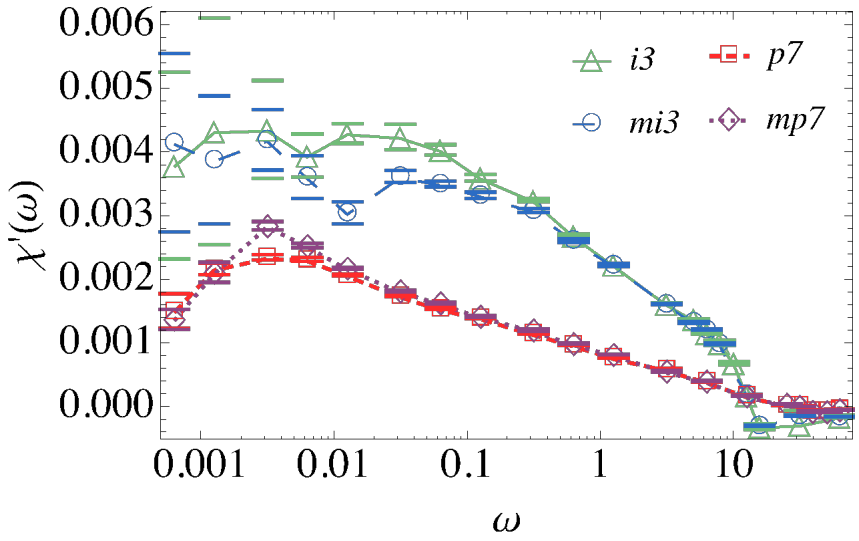


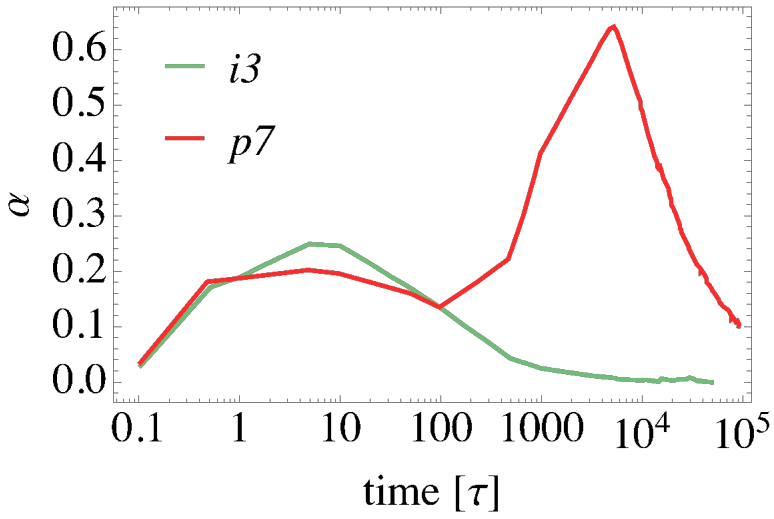
scales as 1/ω as ω → 0

conductivity agrees with static calculation

Lower Frequencies

$$P_x(\omega,t) = \frac{e}{V}\sum_i z_i r_{x,i} = \chi^*(\omega)E_x(\omega,t)$$





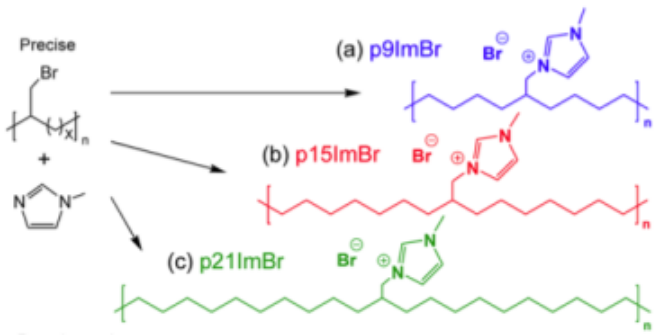
cluster relaxation times from S(k,t)

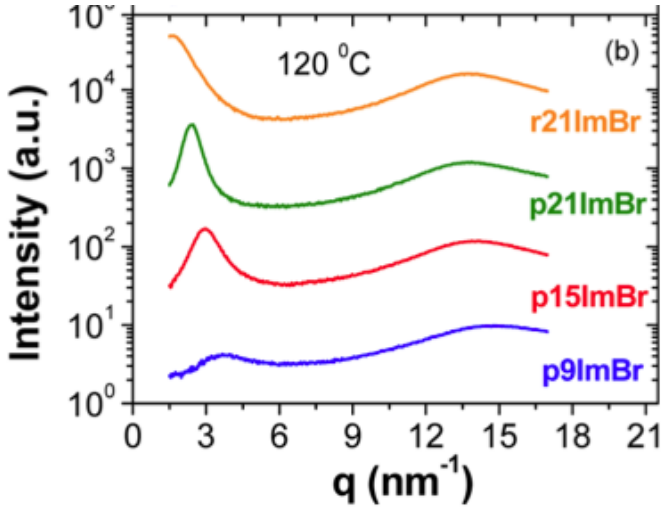
iN3 $1/\tau^* \approx 0.02/\tau$
pN7 $1/\tau^* \approx 0.0001/\tau$

- can't resolve cluster rearrangements in p7
- do see chain/cluster dynamics in i3, mi3

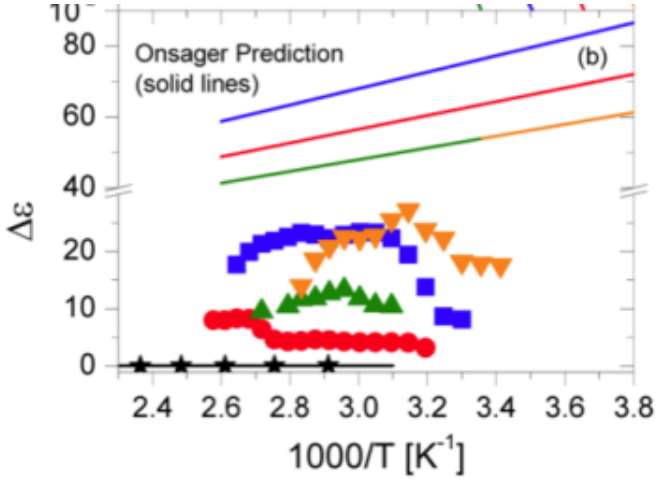
Compare to Experiment

precise PE-ImBr ionomers





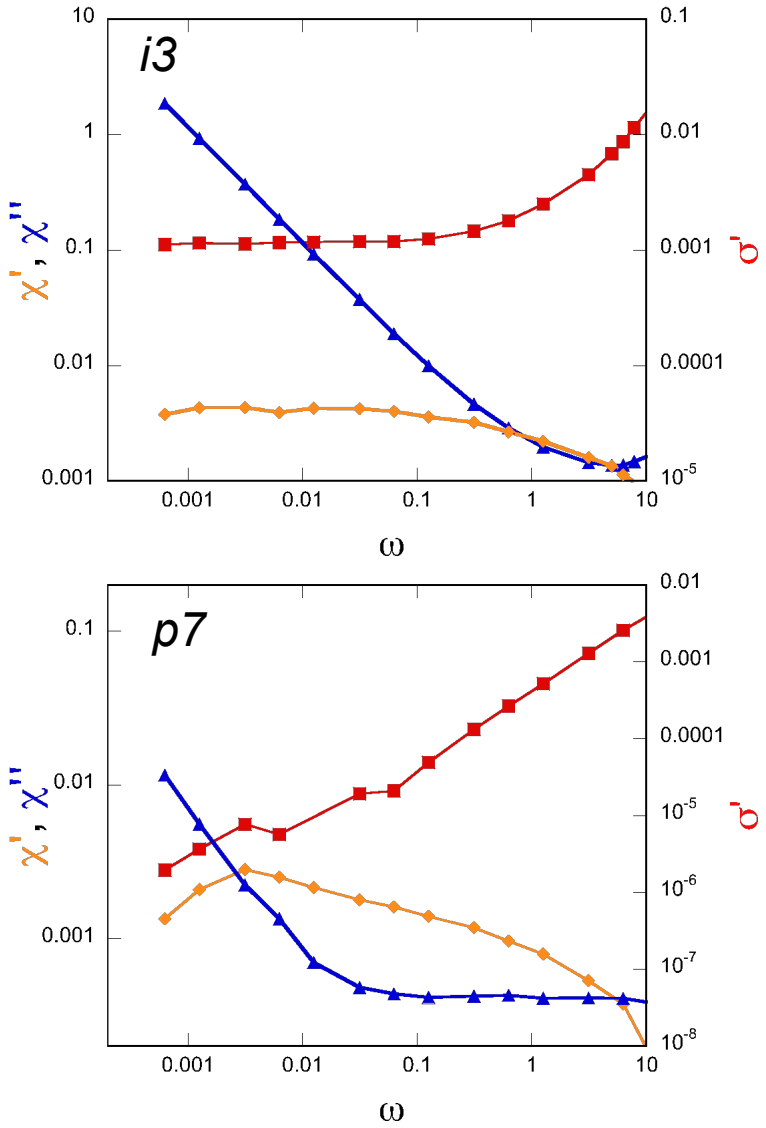
dielectric strength of α process

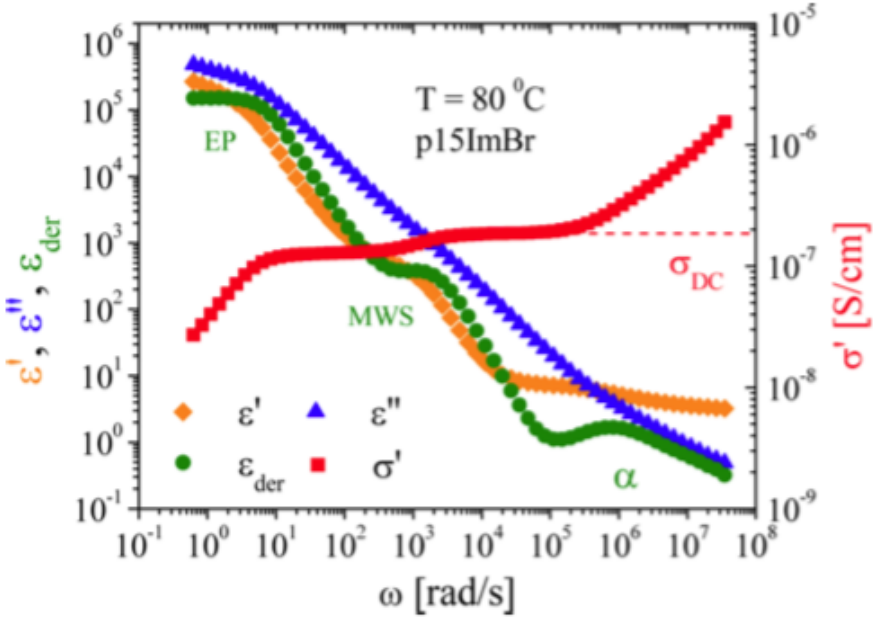


- ImBr form ionic aggregates
- dielectric response primarily due to ions
- some fraction of ions participate in α process

Choi, U. H. *et al. Macromolecules* **48,** 410–420 (2015)

Compare to Experiment





simulations too noisy to resolve α process
shapes of spectra similar to experiment

Conclusions

- molecular architecture important
  - isolated aggregates for pendants or large spacing
  - percolation for ionenes or short spacing
- ion motion by cluster rearrangment
- ion motion is correlated
- higher conductivity in percolated morphologies
- methodology for extracting $\sigma(\omega)$, $\chi(\omega)$ from simulations

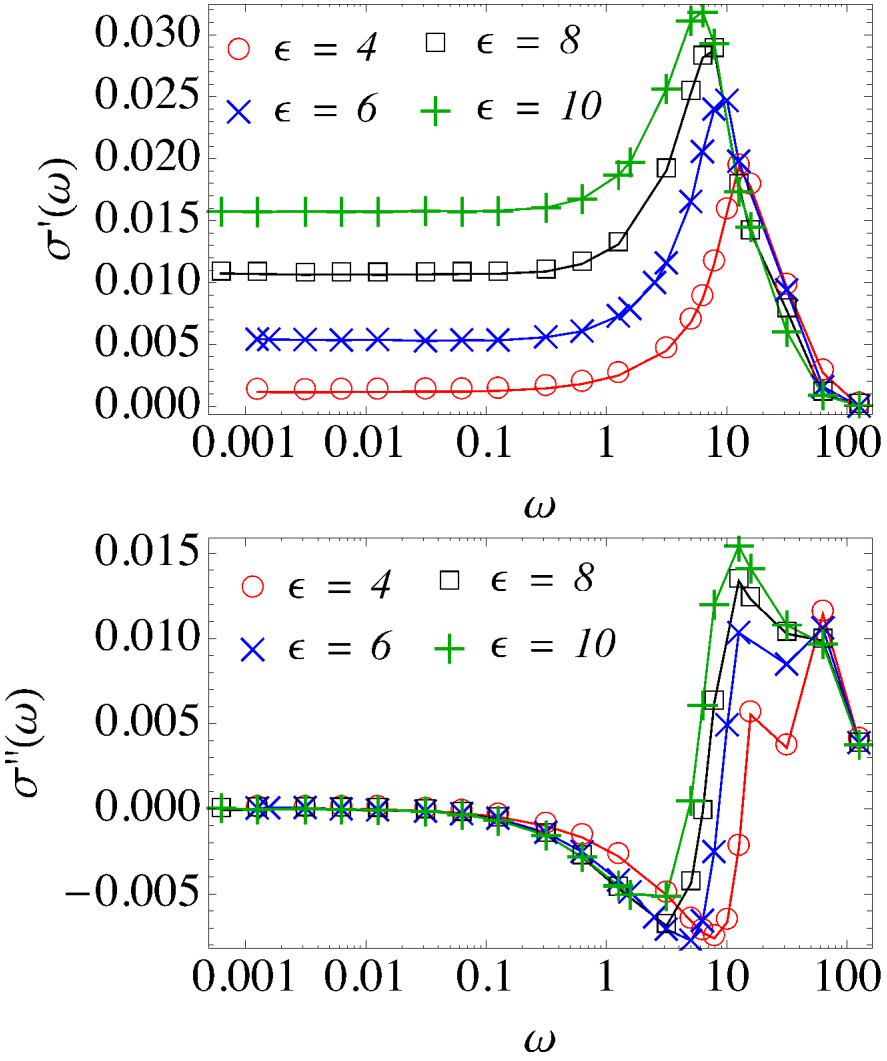
coarse-grained

Hall, et al., *Phys Rev Lett* 106, 127801 (2011);
JACS 134, 574 (2012);
Macromolecules, 45, 8097 (2012);
Ting et al., *Macromolecules* 48, 809 (2015);
Ting et al., in preparation (2016)

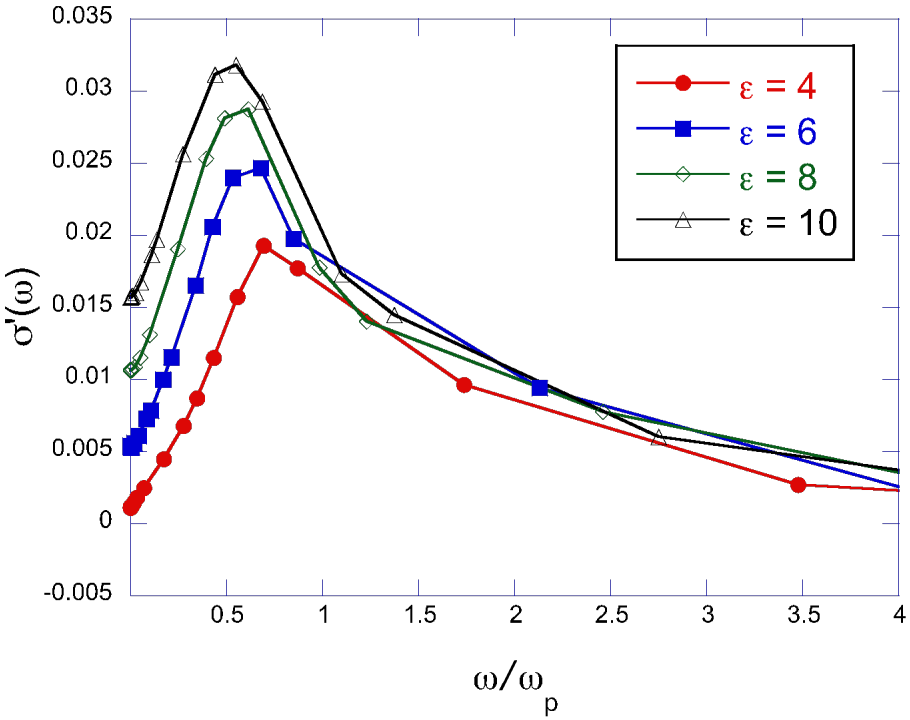
atomistic

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);
Buitrago et al., *Macromolecules* 48, 1210 (2015)

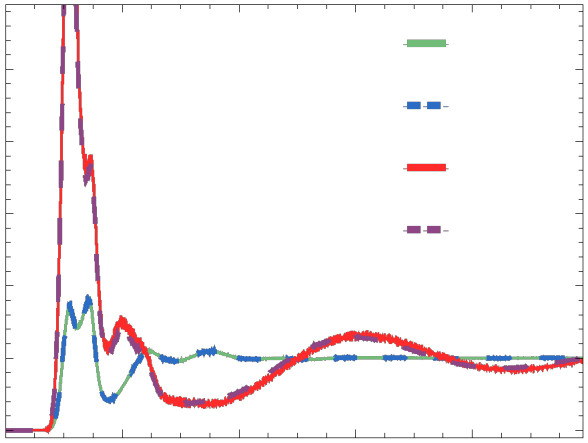
Dependence on ε: iN3



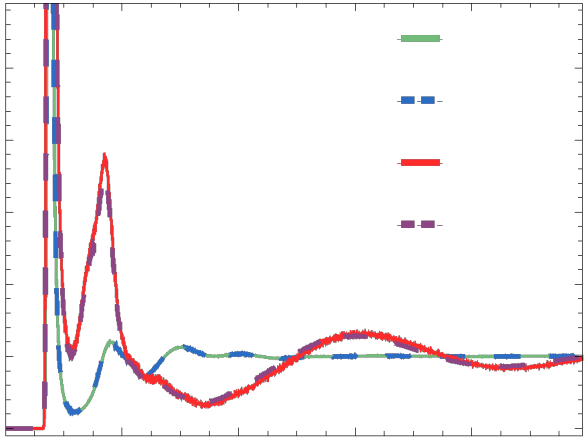
linear scale, normalize by ω_p



Monomer vs Ionomer Structure

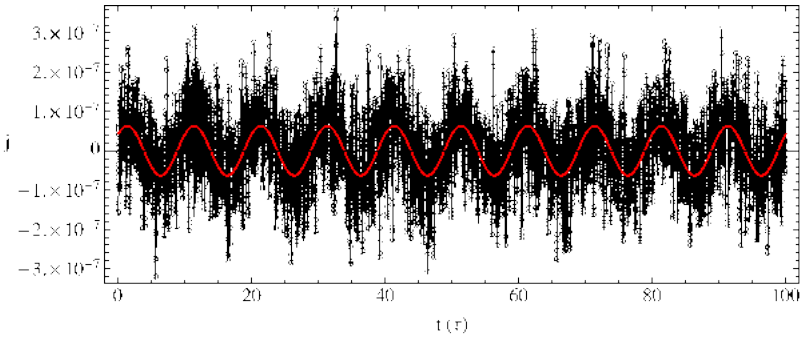


$[\sigma]$

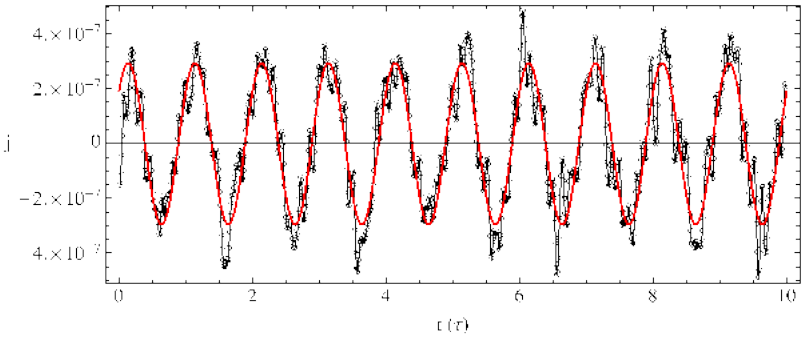


$[\sigma]$

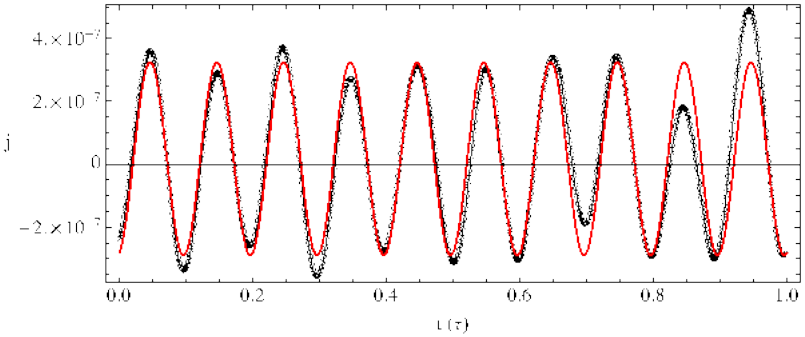
Current Density



$\omega = 0.1/\tau$



$\omega = 1.0/\tau$



$\omega = 10.0/\tau$

i3 system

$\omega_p = 14.2/\tau$

Cluster Dynamics

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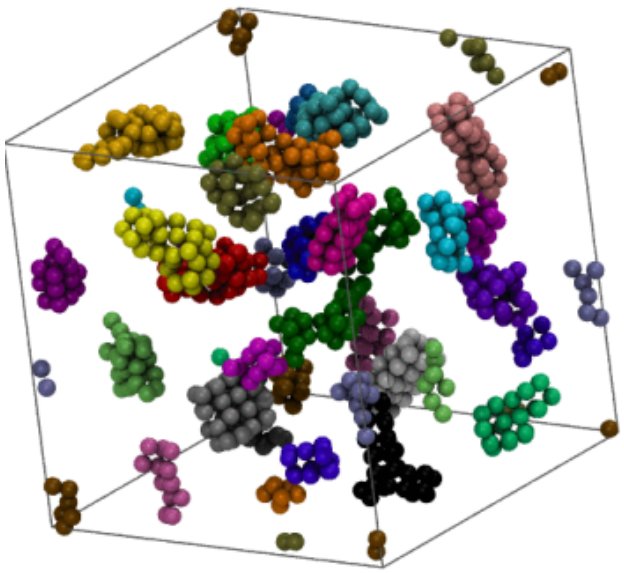
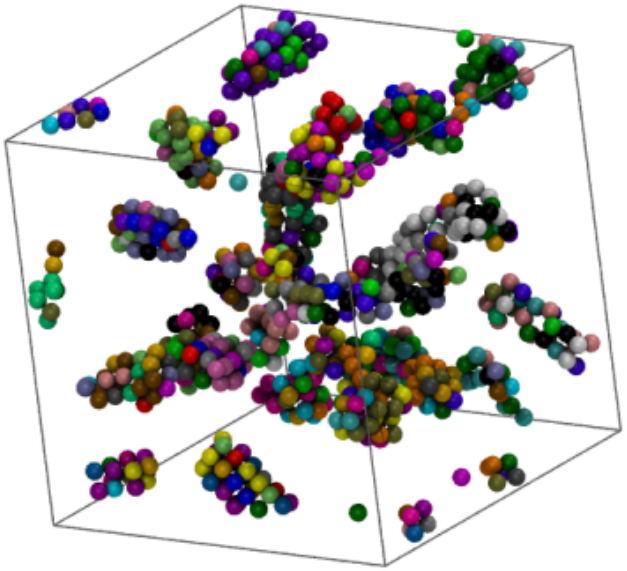
Is there any?

Color distinct clusters by different color

Start



Finish (10^7 steps later)
$t = 50{,}000\ \tau$



Ions move.

Cluster Dynamics

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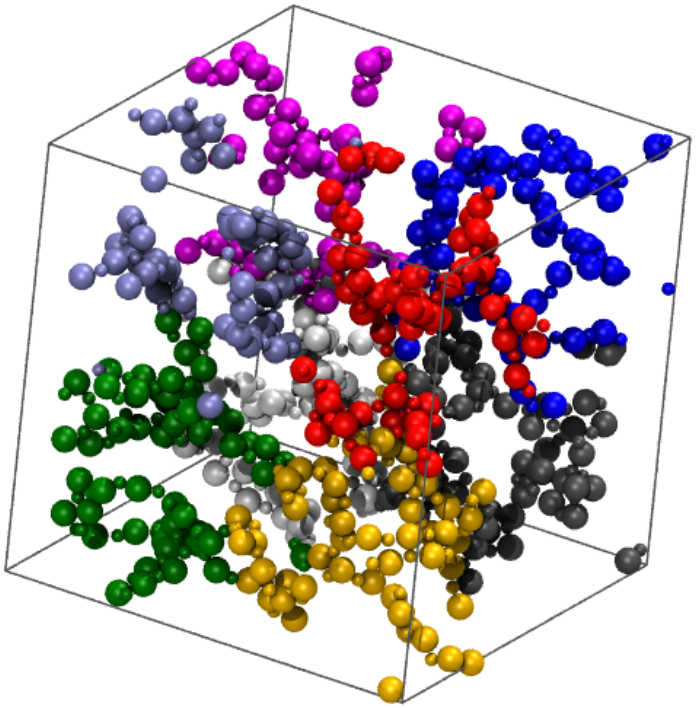
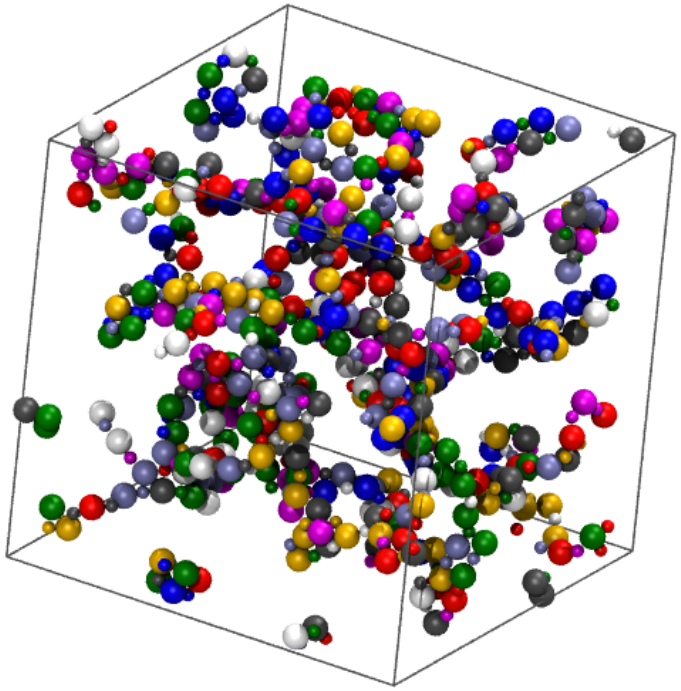
ionenes

Start

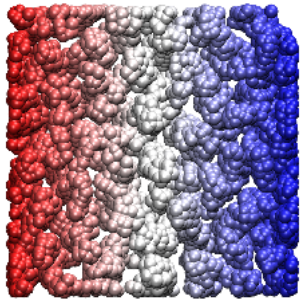


Finish (10^7 steps later)



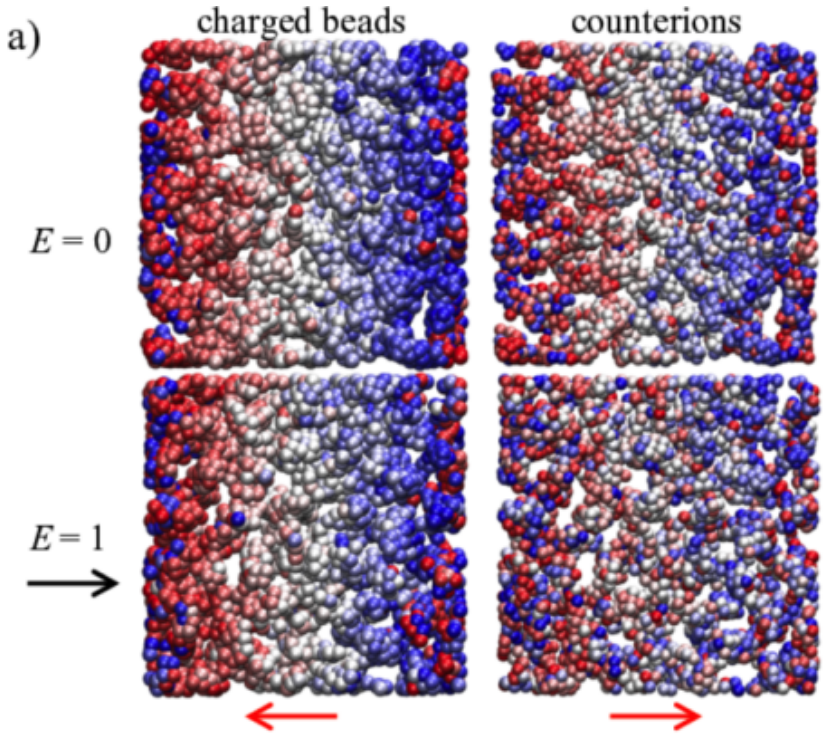
Field does not enhance mixing

t = 0



pendants, N = 9

t = 7.5 x 10^4 τ , $\langle r_x^2 \rangle_0 \approx 25$



- field biases ion motion in field direction
- mixing occurs once $\langle r_x^2 \rangle_0 \approx 100$
  - independent of field
  - mixing by thermal motion

Molecular Dynamics Simulations

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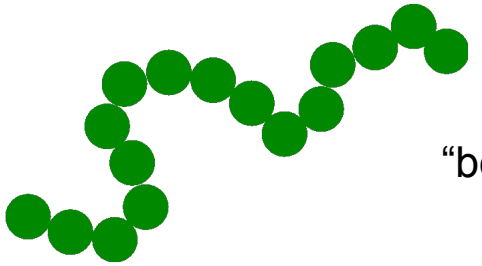
bead-spring polymer model
(Kremer & Grest, 1990)

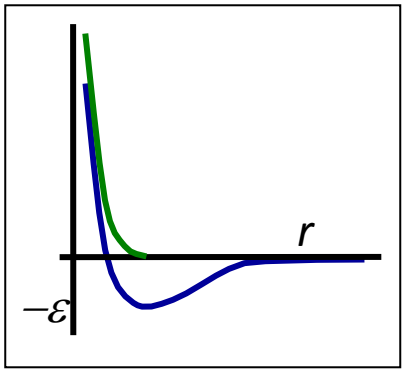


"bead" diameter σ

interactions between all "beads"

Lennard-Jones potential:

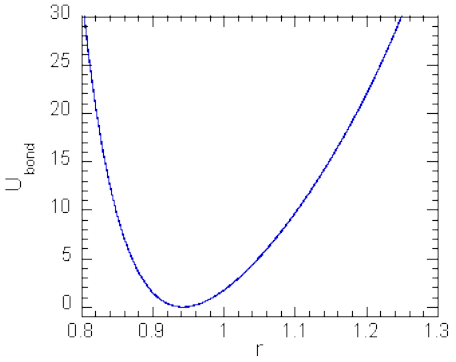
$$u_{LJ} = 4\varepsilon\left[\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^{6}\right]$$



interactions between bonded beads

FENE springs $u(r) = -kR_0^2 \ln\left(1 - (r/R_0)^2\right)$

$U_{bond} = u_{LJ} + u$



+ Coulomb interactions

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

+ temperature

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

Morphology: Li-neutralized pAA

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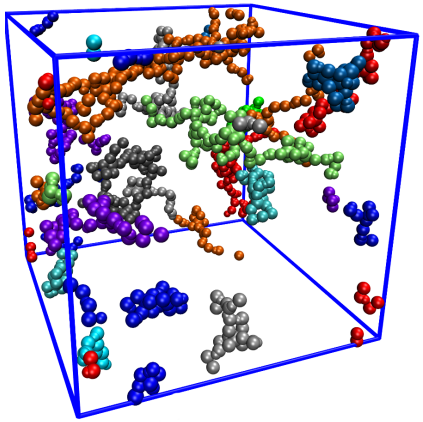
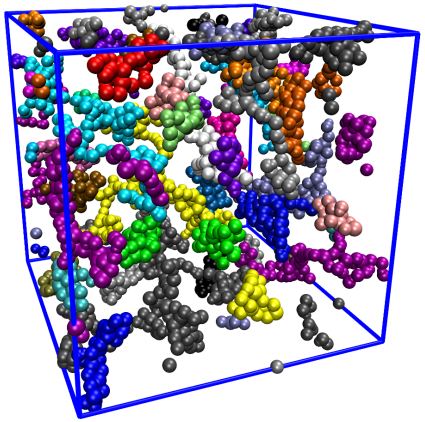
coloring by cluster

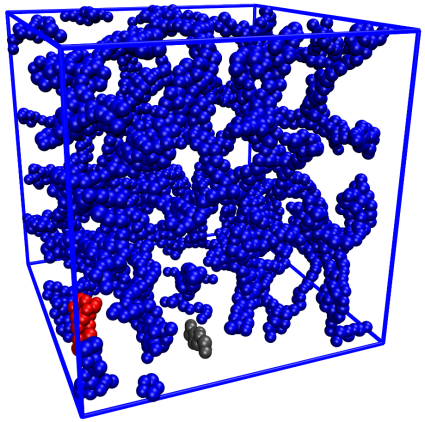
p9AA-10%Li



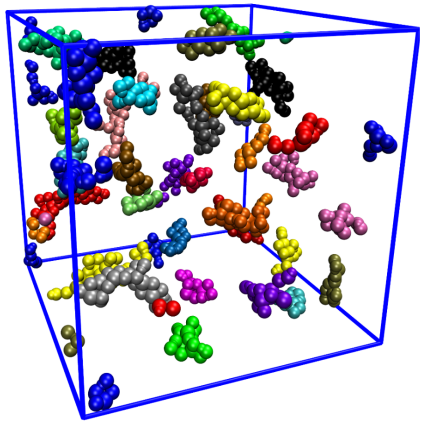
p9AA-43%Li



p9AA-100%Li



p21AA-43%Li



Bolintineanu et al, *ACS Macro Lett*, 2013

Closer look at aggregates

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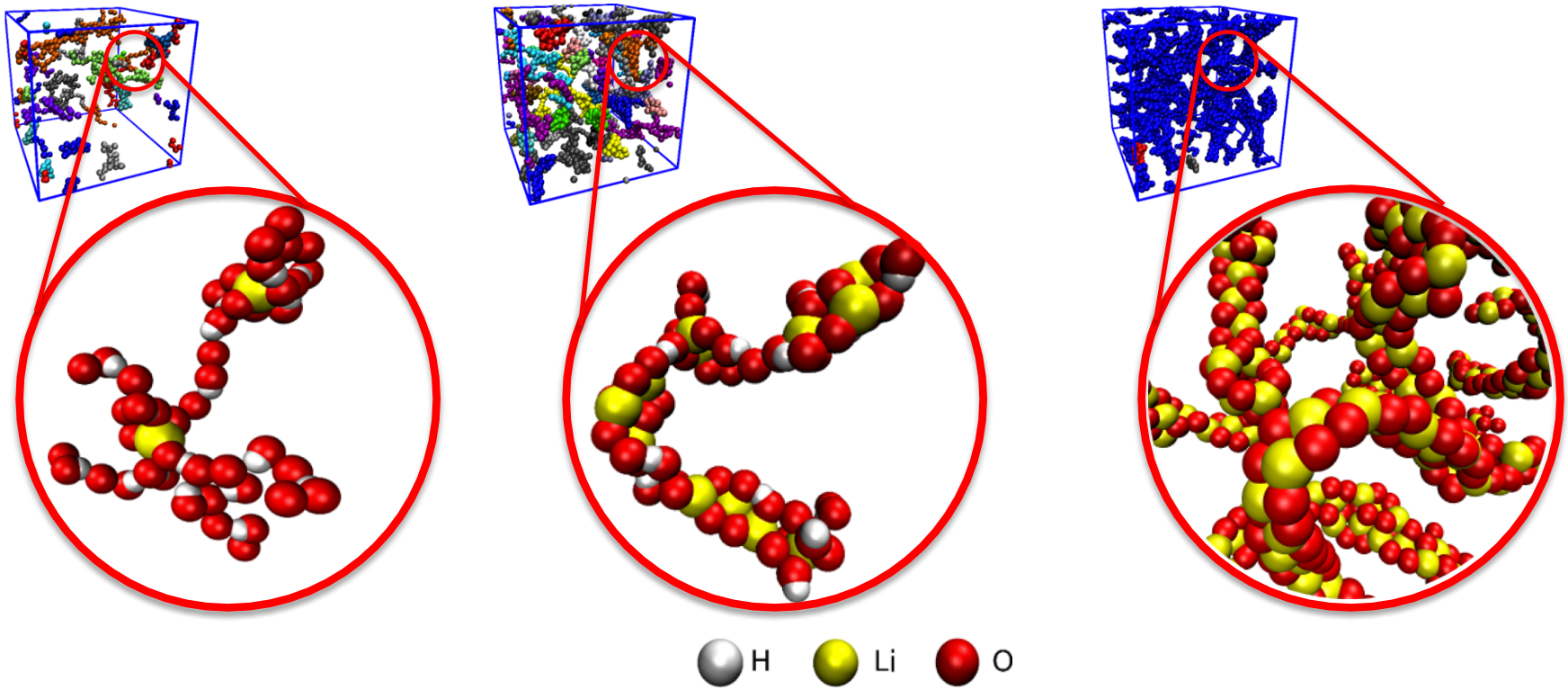
p9AA-10%Li

p9AA-43%Li

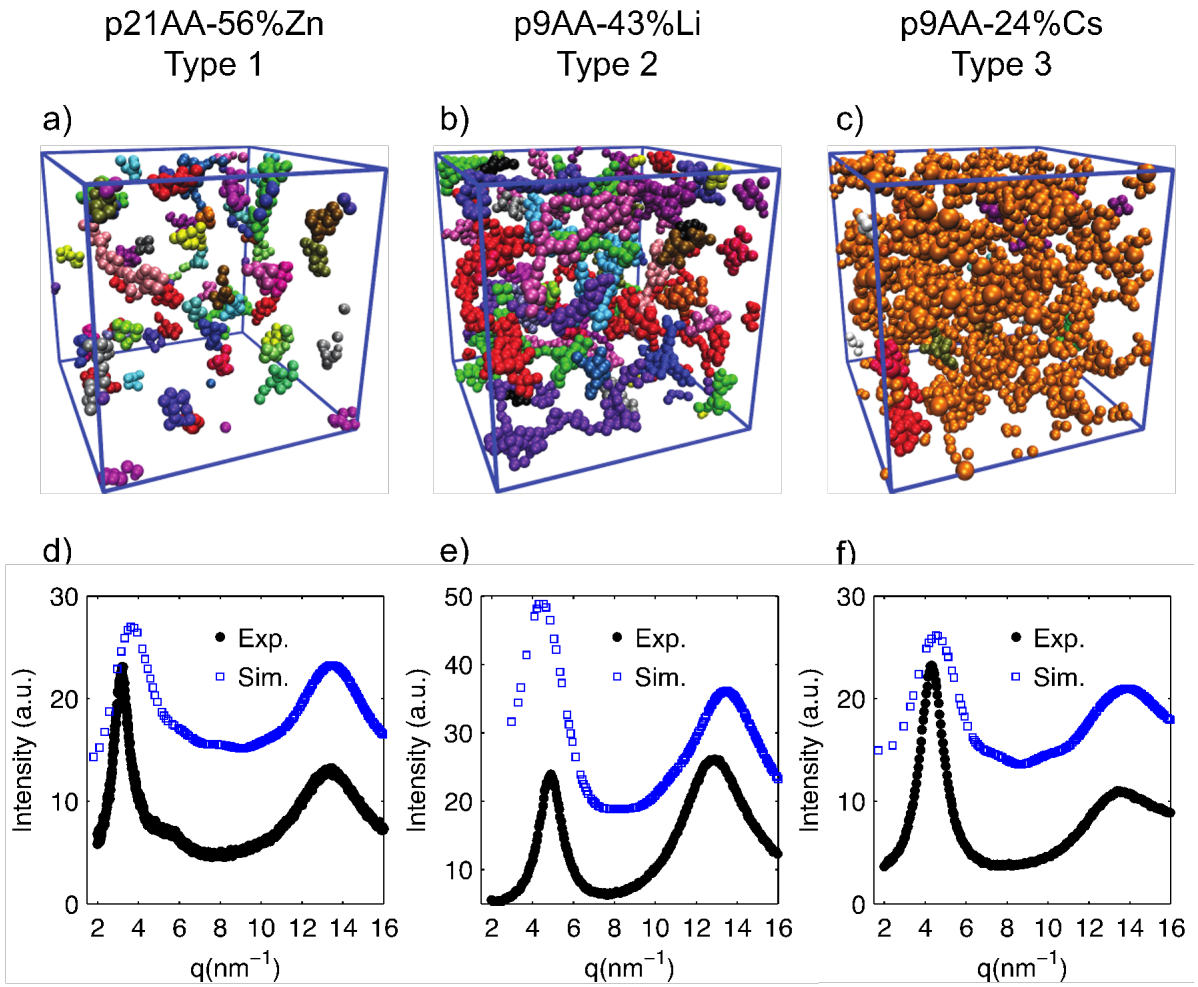
p9AA-100%Li



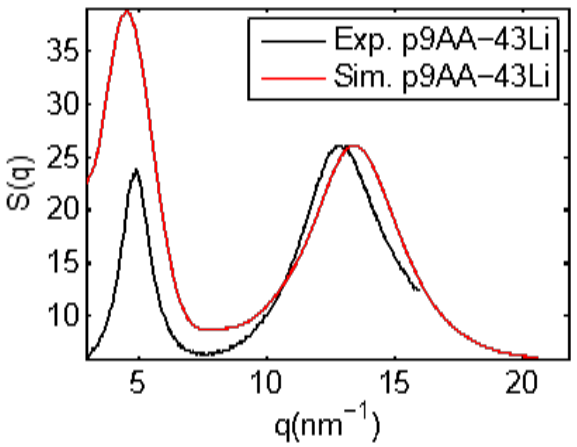
Two mechanisms of aggregate formation:

1. Counterion-oxygen association → dominant at **moderate to high** neutralization
2. Hydrogen-bonded networks → dominant at **low** neutralization

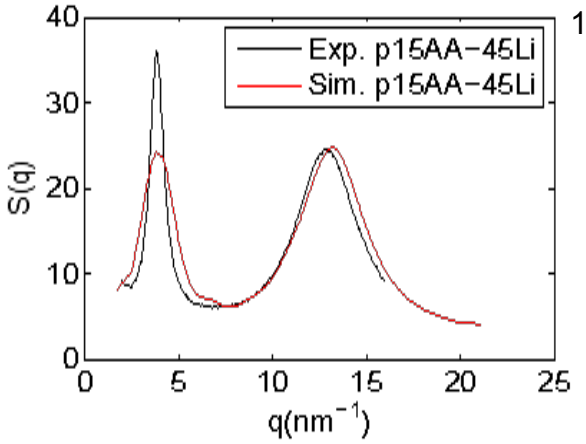
Comparison to X-ray Scattering



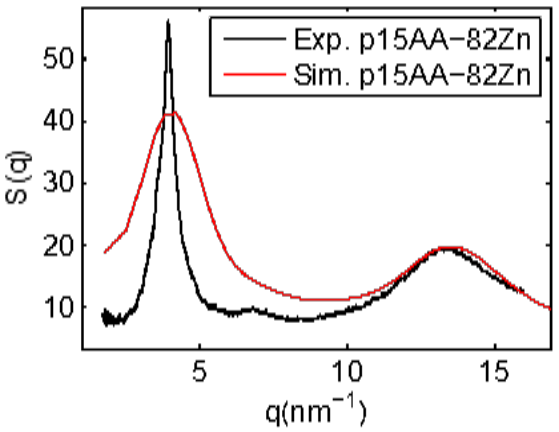
Direct Comparison



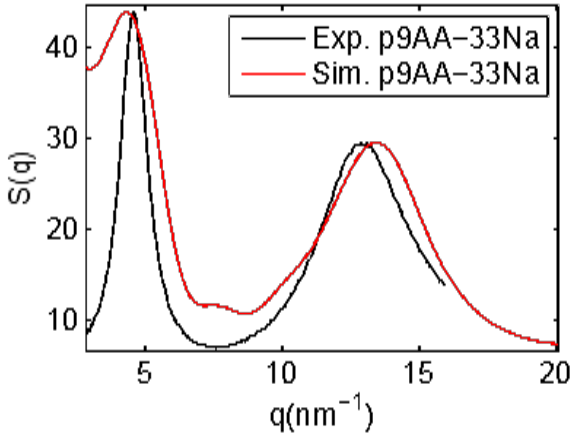
[1]



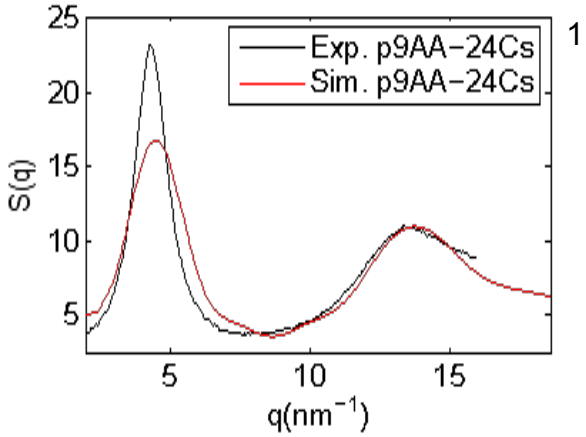
[1]



[2]



[1]



[1]

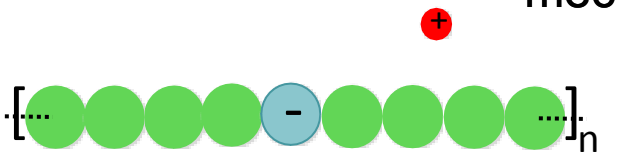
- 120°C, same neutralization
- S(q) scaled to match amorphous halo height

[1] Buitrago et al, Macromolecules 48, 1210 (2015)
[2] Seitz et al, JACS 132, 8165 (2010)

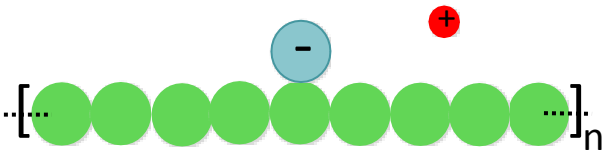
- excellent agreement in peak positions
- good agreement in peak shapes

Ion Trajectories

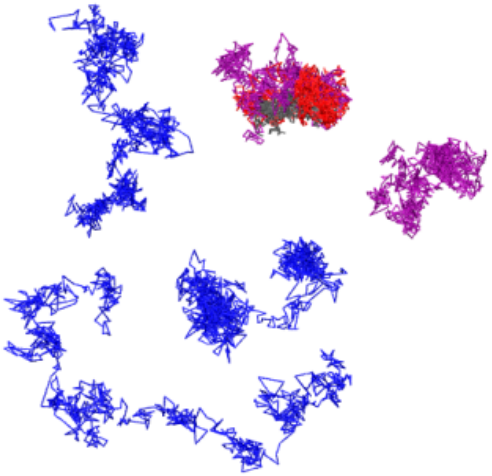
mechanism is not standard hopping



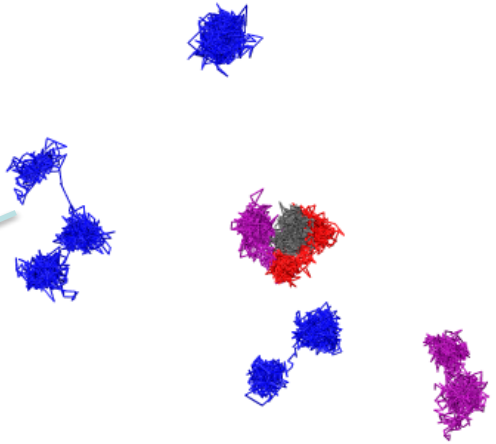
periodic ionenes N = 9



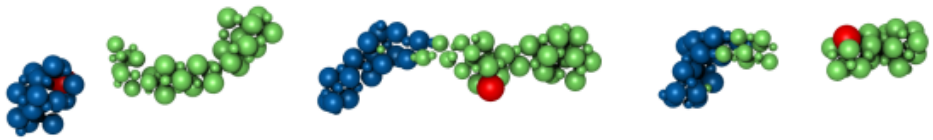
periodic pendants N = 9



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)



Static Electric Field

Sandia National Laboratories

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 = 8×10^6 V/cm

Ionomer MD Simulations

Sandia National Laboratories

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