SAND2014-1902C

Coarse-grained ionomer melts under an external electric field

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APS March Meeting
March 5, 2014

Ionomers

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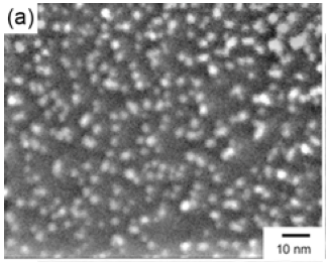
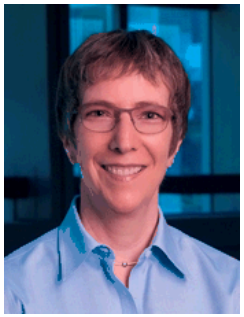
Polymers with small fraction of charged groups

- ion-ion interactions + low dielectric polymer

→ ionic aggregates

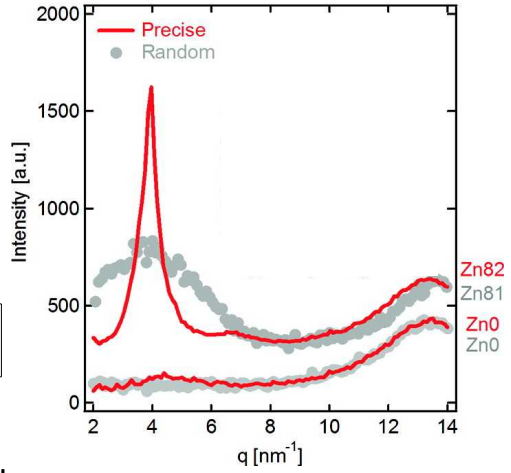




Karen Winey, Penn

Precise ionomers:

Synthesize by acyclic diene metathesis (ADMET)



- What do the aggregates look like?
- What is the dependence on polymer architecture?
- How does this affect ion dynamics?

Ken Wagener, U Florida

Coarse-grained MD simulations

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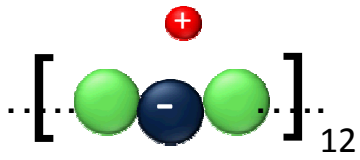
charged groups in the backbone:

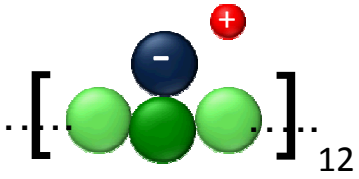
"ionene"

charged groups pendant to the backbone:

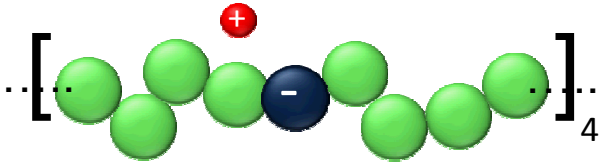
"pendant"

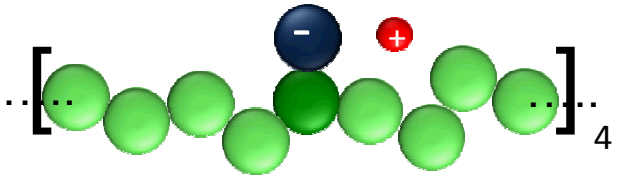
N_{bb} = 3





N_{bb} = 9

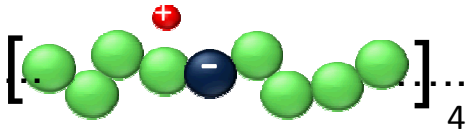


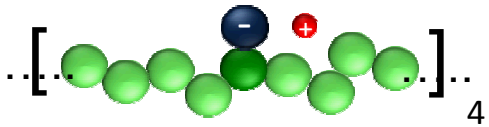


repulsive LJ interactions
+ FENE bonds
+ coulomb interactions: $U(r) = \frac{q_1 q_2}{4\pi\epsilon_0 \epsilon r}$
+ Langevin thermostat

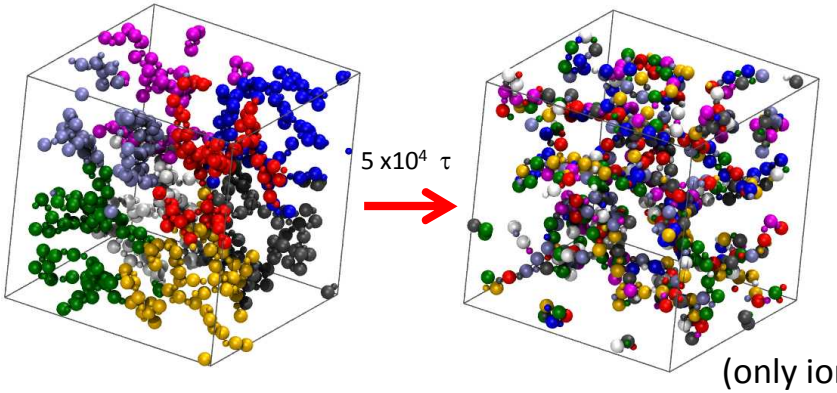
Simulation details:
800 polymers
100% neutralization
bulk dielectric constant = 4
counterion size = 0.5σ
Bjerrum length = 35.7σ

Aggregate structure and dynamics

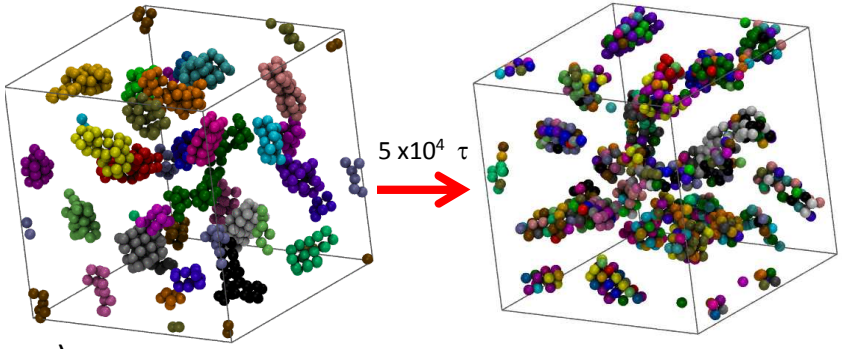
ionene, $N_{bb} = 9$ 

pendant, $N_{bb} = 9$ 

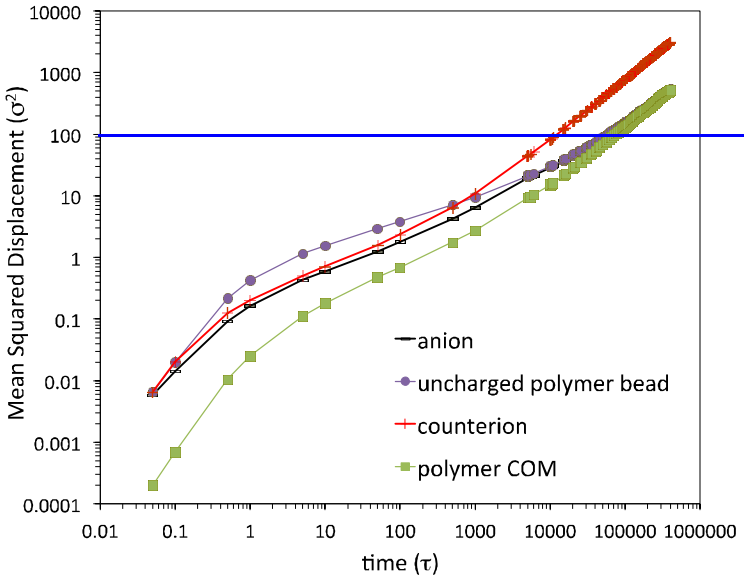
Percolated clusters

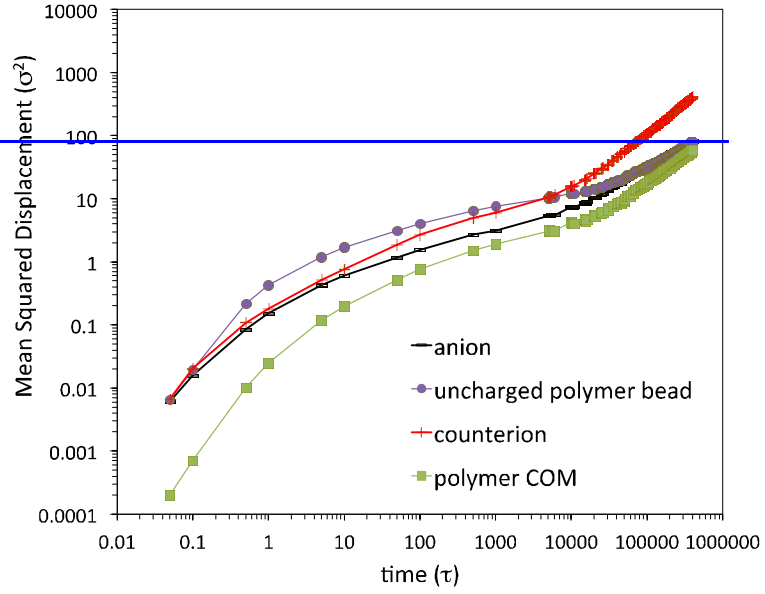


Not percolated: discrete compact clusters



(only ions shown)





Structure: Hall et al., *Phys. Rev. Lett.* (2011); Hall et al., *J. Am Chem. Soc.* (2012) Dynamics: Hall et al., *Macromolecules.* (2012)

How strong a field should we add?

$$E^* = \frac{kT}{q\sigma} = 1$$

Adds force $F_x = qE_x$ to each ion $\longrightarrow$ $F = 1/kT\sigma$

Compare with electrostatic force between two ions at contact:

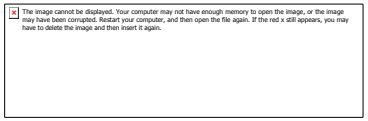
$$\frac{F}{kT\sigma} = -\frac{q_i q_j}{r^2}\frac{\ell_B}{\sigma} \qquad \begin{array}{l} l_B/\sigma = 35.7 \\ r = 0.75\sigma \end{array}$$

$$F = -63/kT\sigma$$

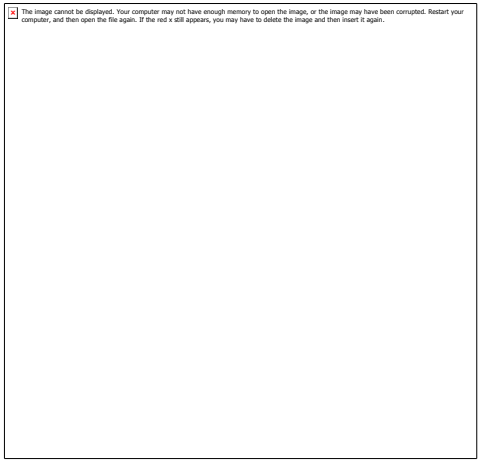
Rough estimate for $E^* = 1$ in real units:

$$\sigma = 0.4\text{nm},\ T = 298\text{K},\ E = 0.8V/\text{nm}$$

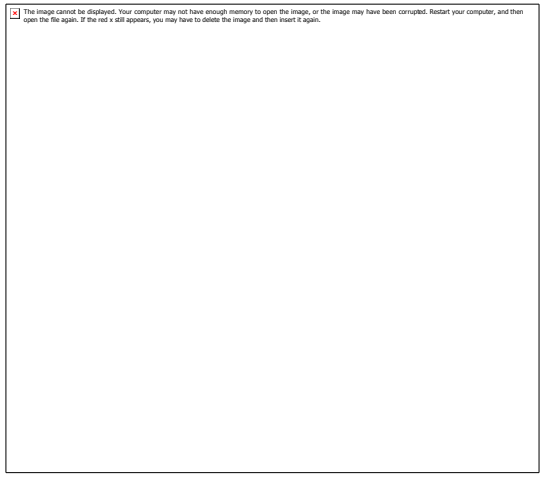
Visualizing field effects on clusters



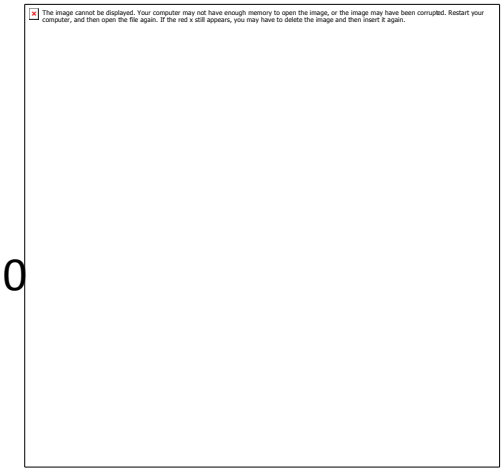
pendants, $N_{bb} = 9$



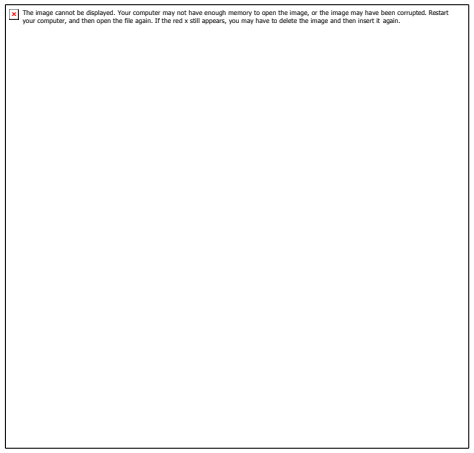
E = 0



after 1.5×10^4 τ



E = 1.0



E = 5.0

Clusters visibly align in high fields

Check Field Strengths

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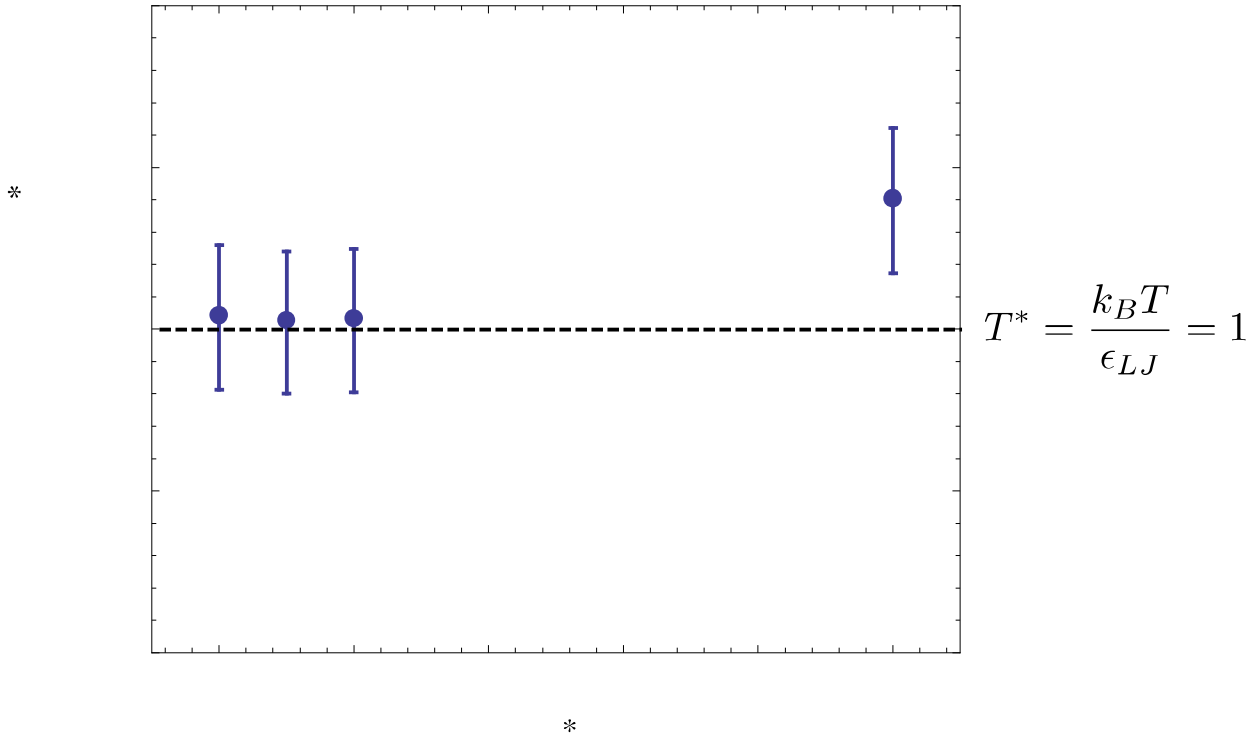
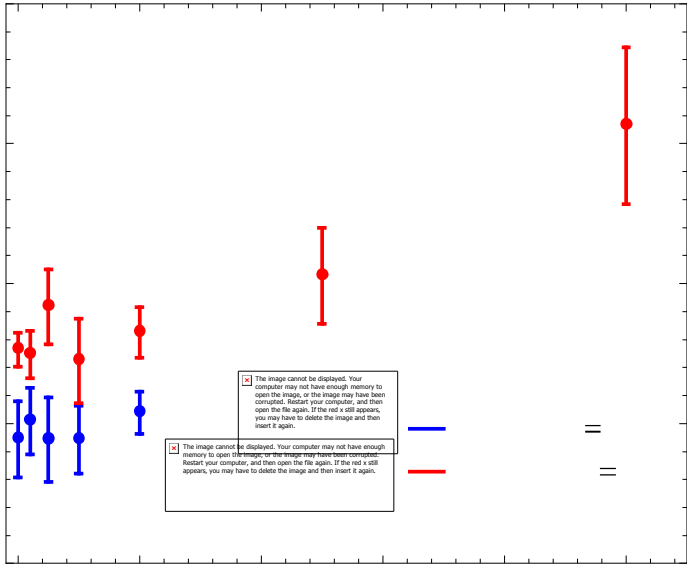
Turn off thermostat in field direction:

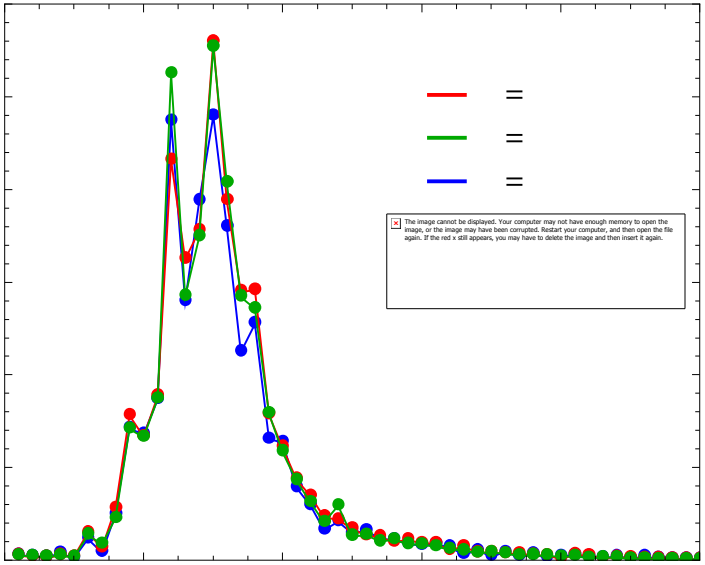


Field effects on structure

Polymer size



Cluster size distribution



no effect on structure for $E \leq 1$

Field effects on dynamics: MSDs

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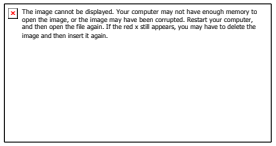
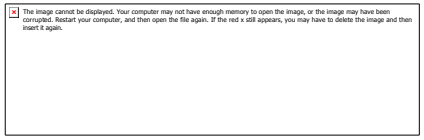


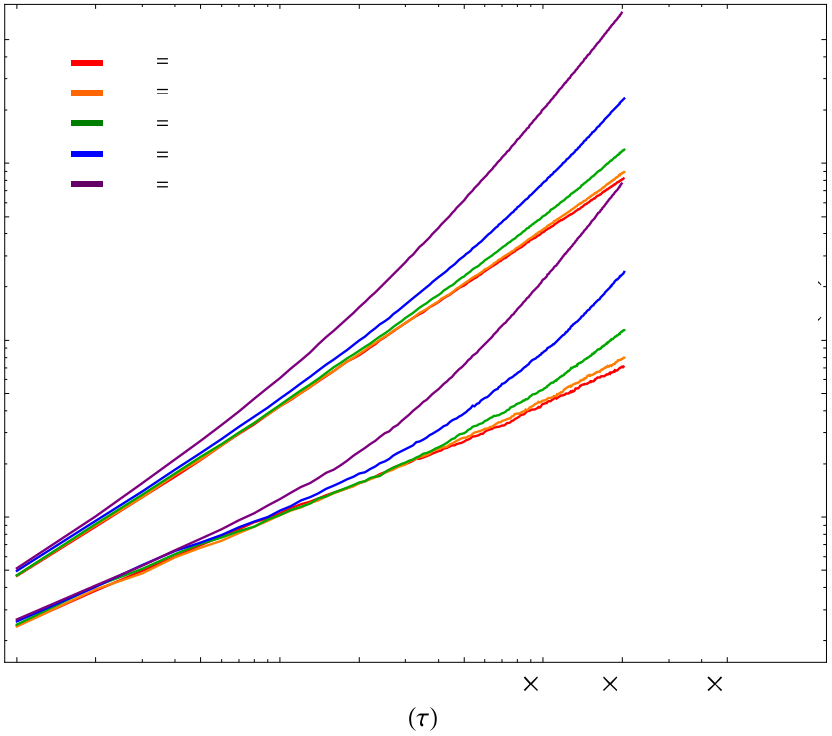
ionene, $N_{bb} = 3$

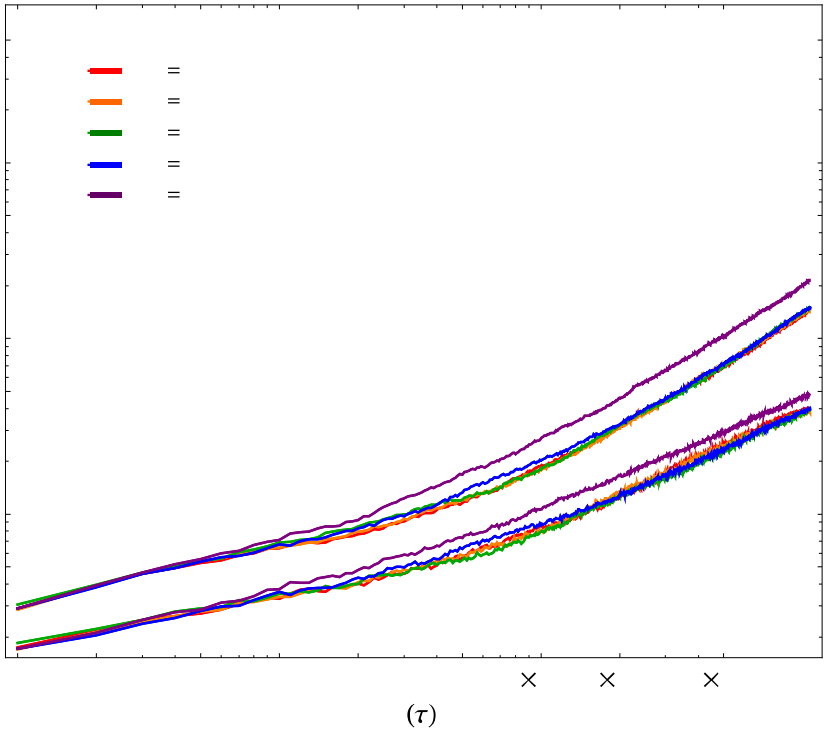
(highest fraction of percolated ions)



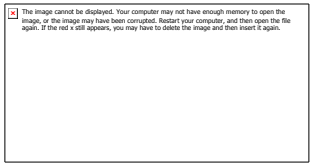
pendant, $N_{bb} = 9$

(discrete ionic aggregates)

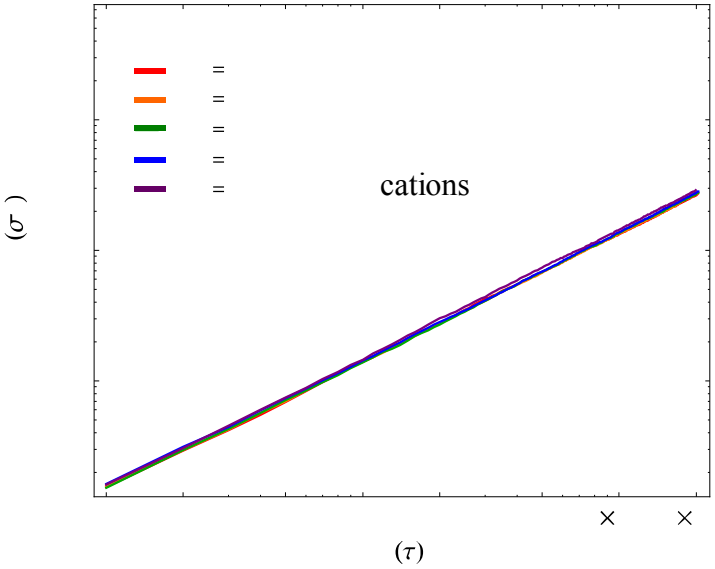




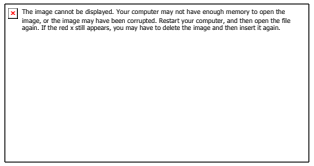
Directional MSDs and the conductivity



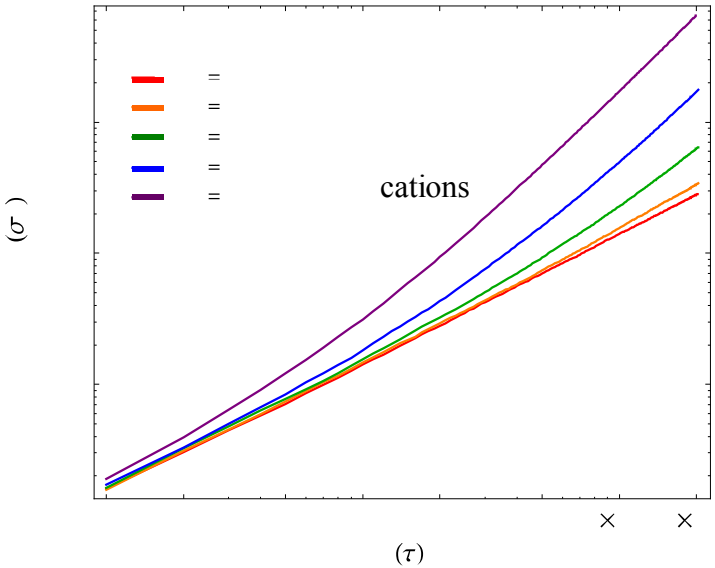
perpendicular to field



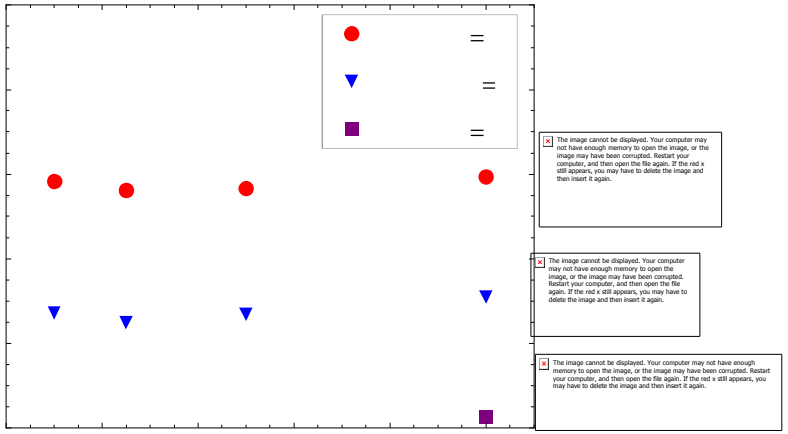
Directional MSDs and the conductivity



in field direction



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



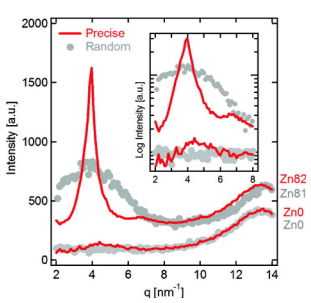
if ions are uncorrelated: $\lambda^{NE} = \frac{e^2\rho}{kT}(D_+ + D_-)$

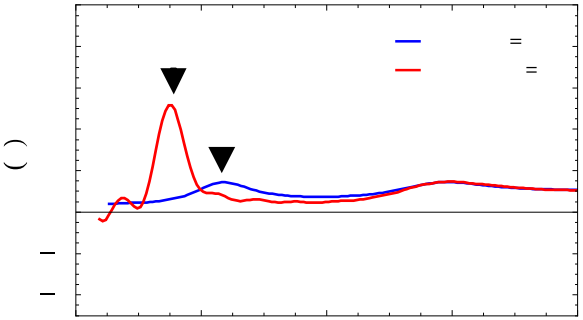
drift velocity: $\langle x_E^2(t)\rangle - \langle x_0^2(t)\rangle = \langle v_x^2\rangle t^2$

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

system	$\alpha = \lambda/\lambda^{NE}$
ionene N = 3	0.36
ionene N = 9	0.18
pendant N = 3	0.36

Time-dependent structure factor



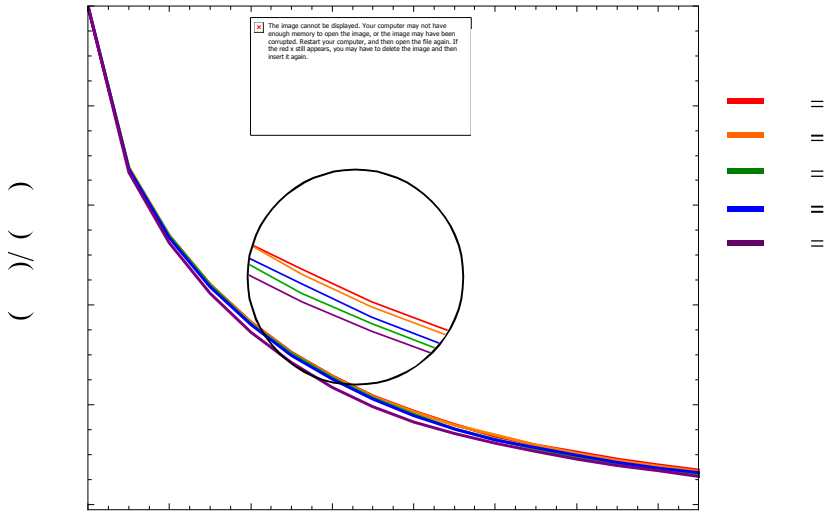


(σ^{-1})

$$S(k,t) = 4\pi\rho \int_0^\infty \frac{\sin(kr)}{kr} r^2 (g(r,t) - 1) dr$$

ionene, N_{bb} = 3

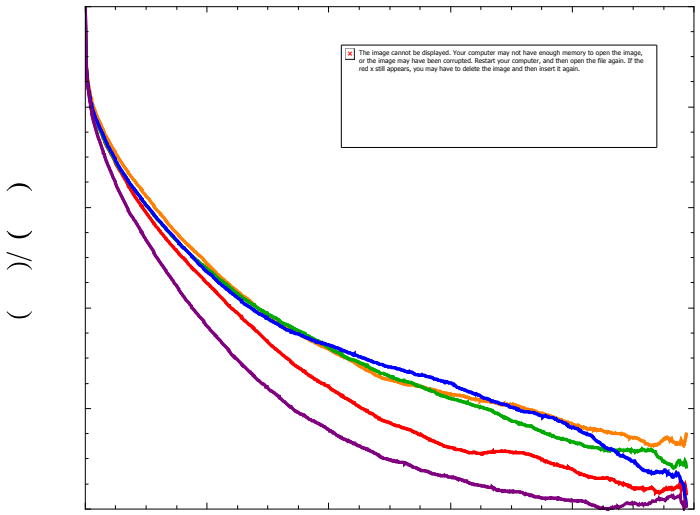
(highest fraction of percolated ions)



(τ)

pendant, N_{bb} = 9

(discrete ionic aggregates)



(τ)

Conclusions and future work

Conductivity is highest for ionene systems, concentration-dependent

Ions are correlated

Field speeds up dynamics and decorrelation clusters for percolated case
Moderate fields slows down decorrelation of discrete, isolated clusters

Analyze cluster trajectories to better understand field effect on dynamics.

Acknowledgements

Lisa Hall (now at OSU)

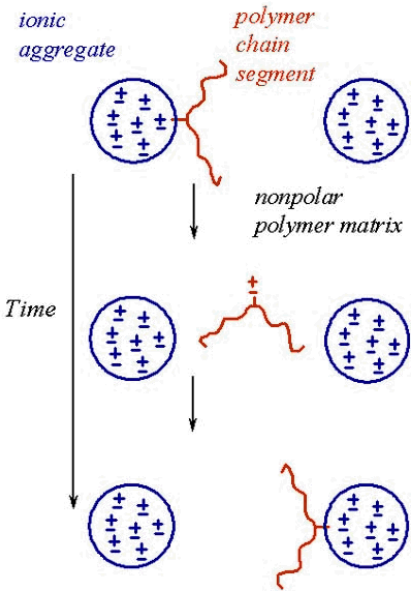
Mark Stevens

Amalie Frischknecht

Harry S. Truman Fellowship
"Ionomers" LDRD team

Aggregate dynamics

historical view vs. simulation view



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ion **pairs** "hop" between aggregates

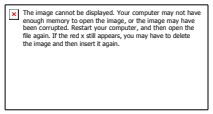
ions move by cluster merging, rearranging, and breaking

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

Field effects on structure

Pair correlation function

ionene, N_{bb} = 3
(highest fraction of percolated aggregates)



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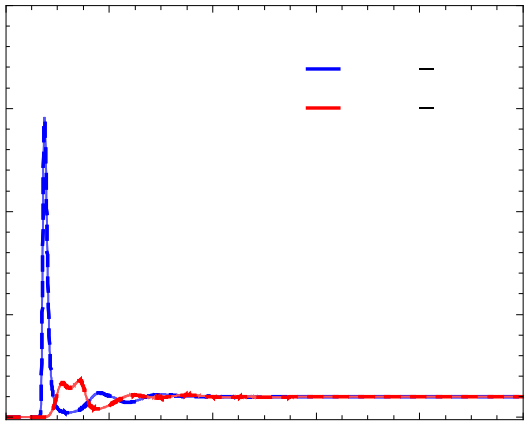

E = 0 (solid)
E = 1.0 (dashed)

pendant, N_{bb} = 9
(discrete aggregates)

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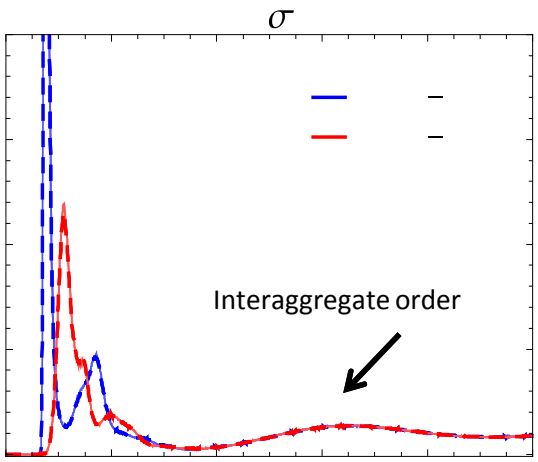
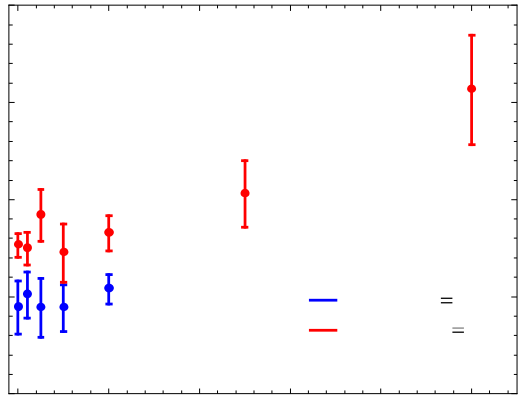


σ

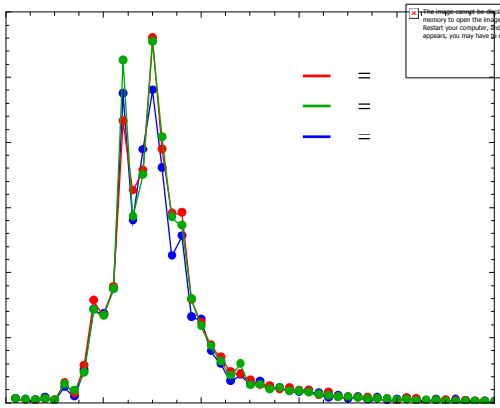
E = 0 (solid)
E = 1.0 (dashed)

σ

Polymer size



Cluster distribution for pendant N_{bb} =9



no effect on structure for E ≤ 1