



Simulations of Coarse-Grained Ionomer Melts in an External Electric Field

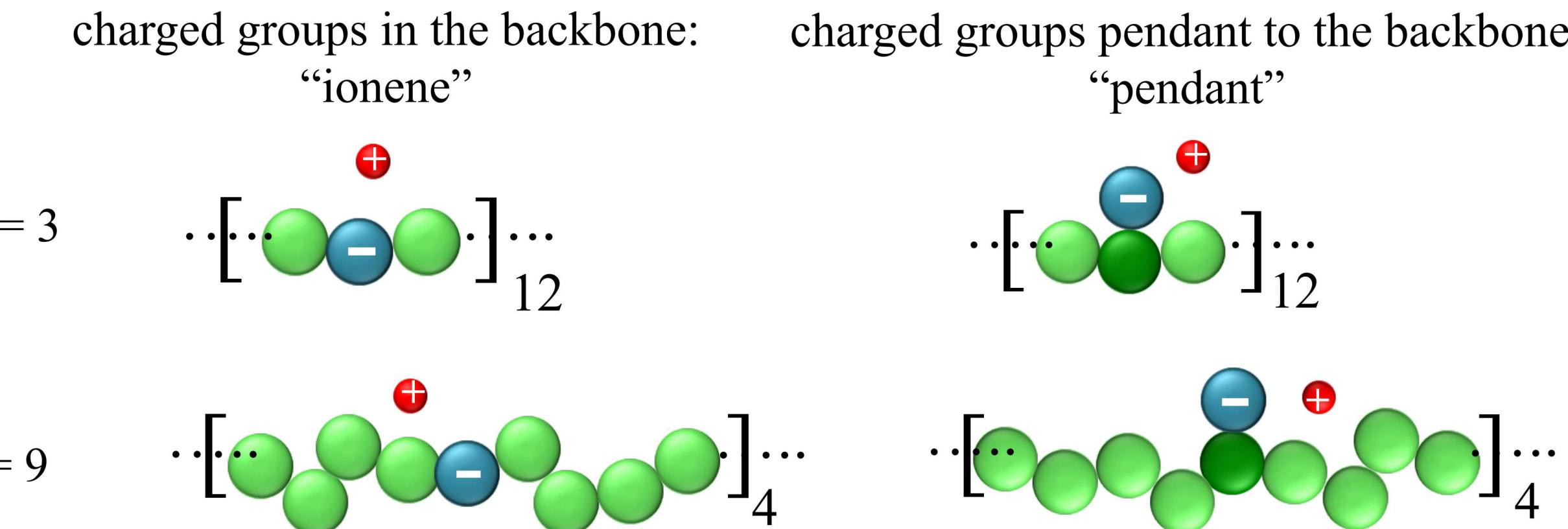
Christina L. Ting, Mark J. Stevens, Amalie L. Frischknecht
 Sandia National Laboratories and Center for Integrated Nanotechnologies

Abstract

Ionomers are polymers that contain both electrically neutral and charged chemical groups, and are being investigated as potential solid electrolytes in batteries. Our group has been investigating structure and dynamics in ionomer melts using molecular dynamics simulations. The overall goal is to understand the relationships among polymer architecture, ionic aggregate morphologies, and ion dynamics. Here we apply an external electric field to coarse-grained models of ionomer melts, which have ionic groups placed either in or pendant to the polymer backbone. In the linear response regime, the field does not affect ionic aggregate morphologies but does affect ion dynamics. The applied field allows us to calculate the ion mobilities and hence the conductivity. A comparison of the conductivity with that calculated by the Nernst-Einstein relation reveals a significant amount of ionic correlation.

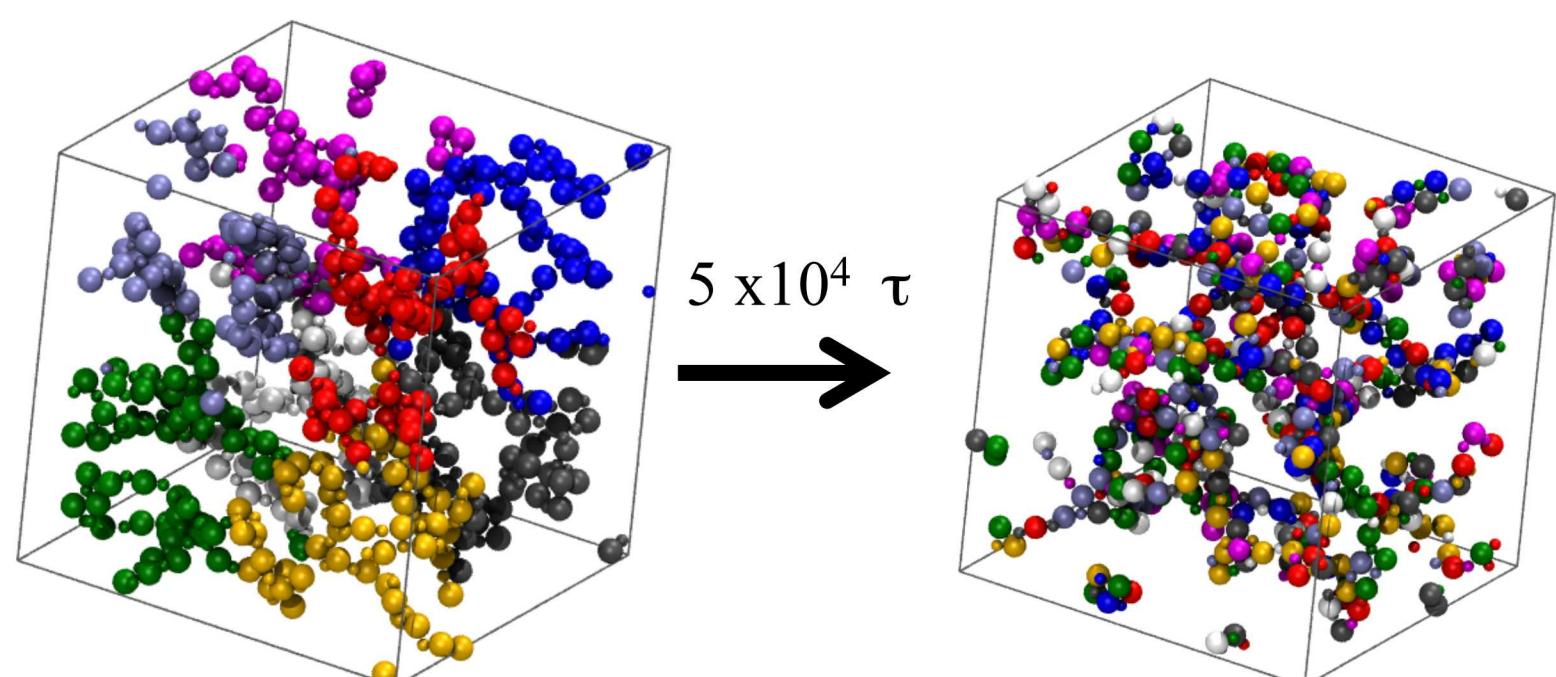
Coarse-Grained MD Simulations

Kremer-Grest bead-spring model with long-ranged coulomb interactions:

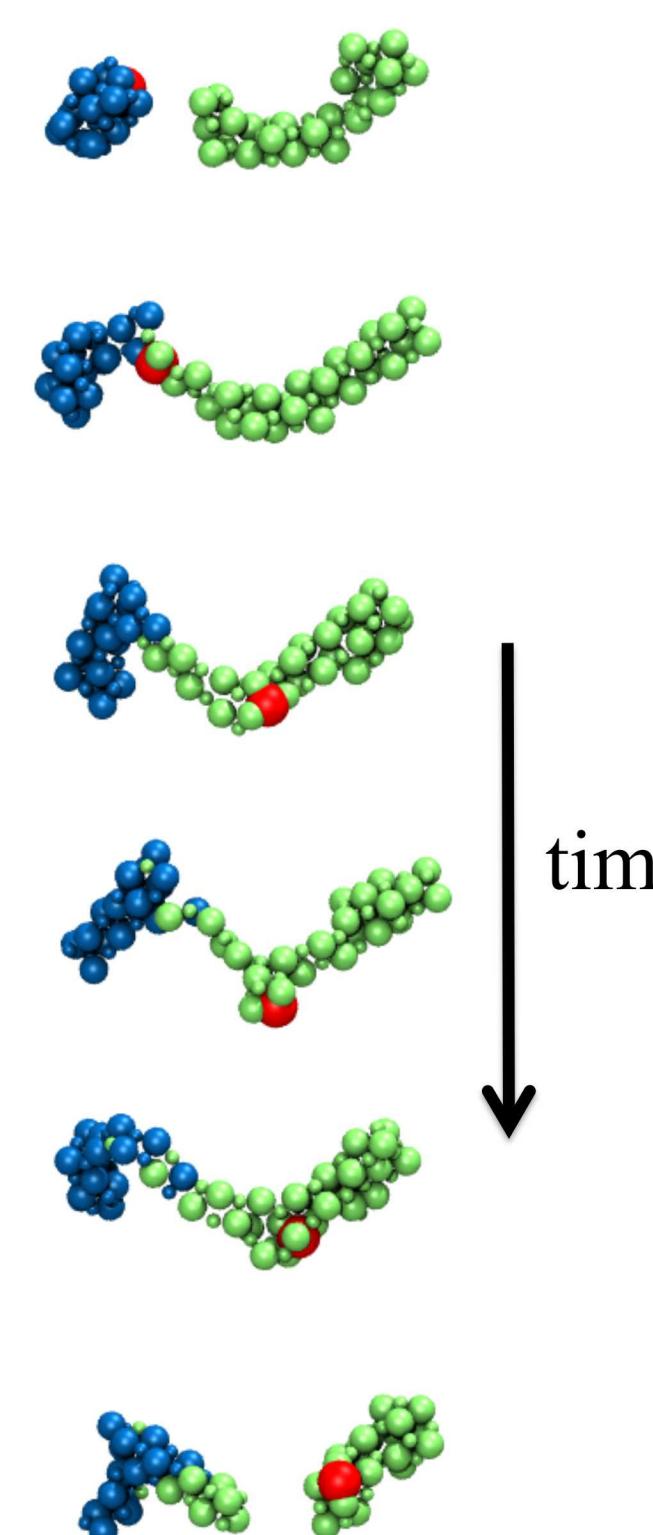


Ionic aggregate morphology and dynamics:

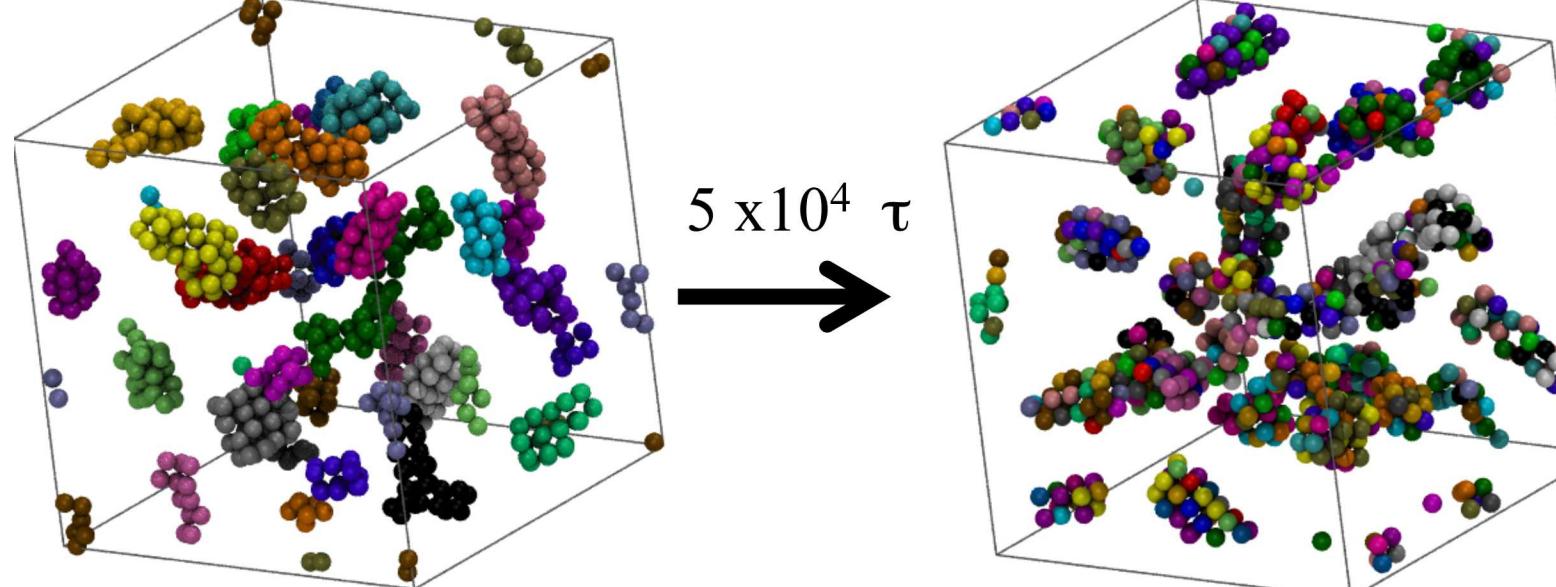
Percolated clusters



ions move by cluster merging/rearrangement



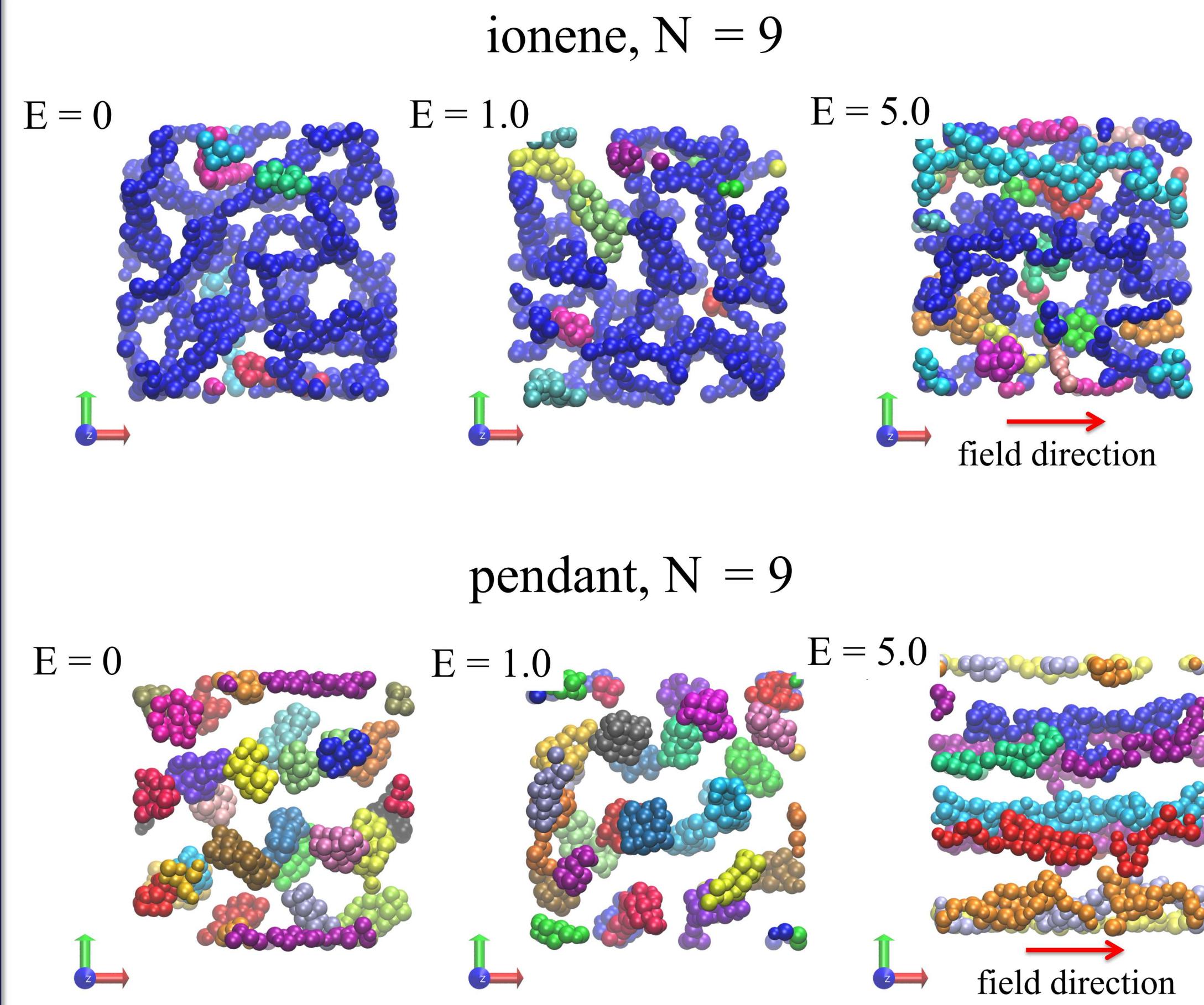
Not percolated: discrete compact clusters



Hall et al., *Macromolecules*, **45**, 8097 (2012)

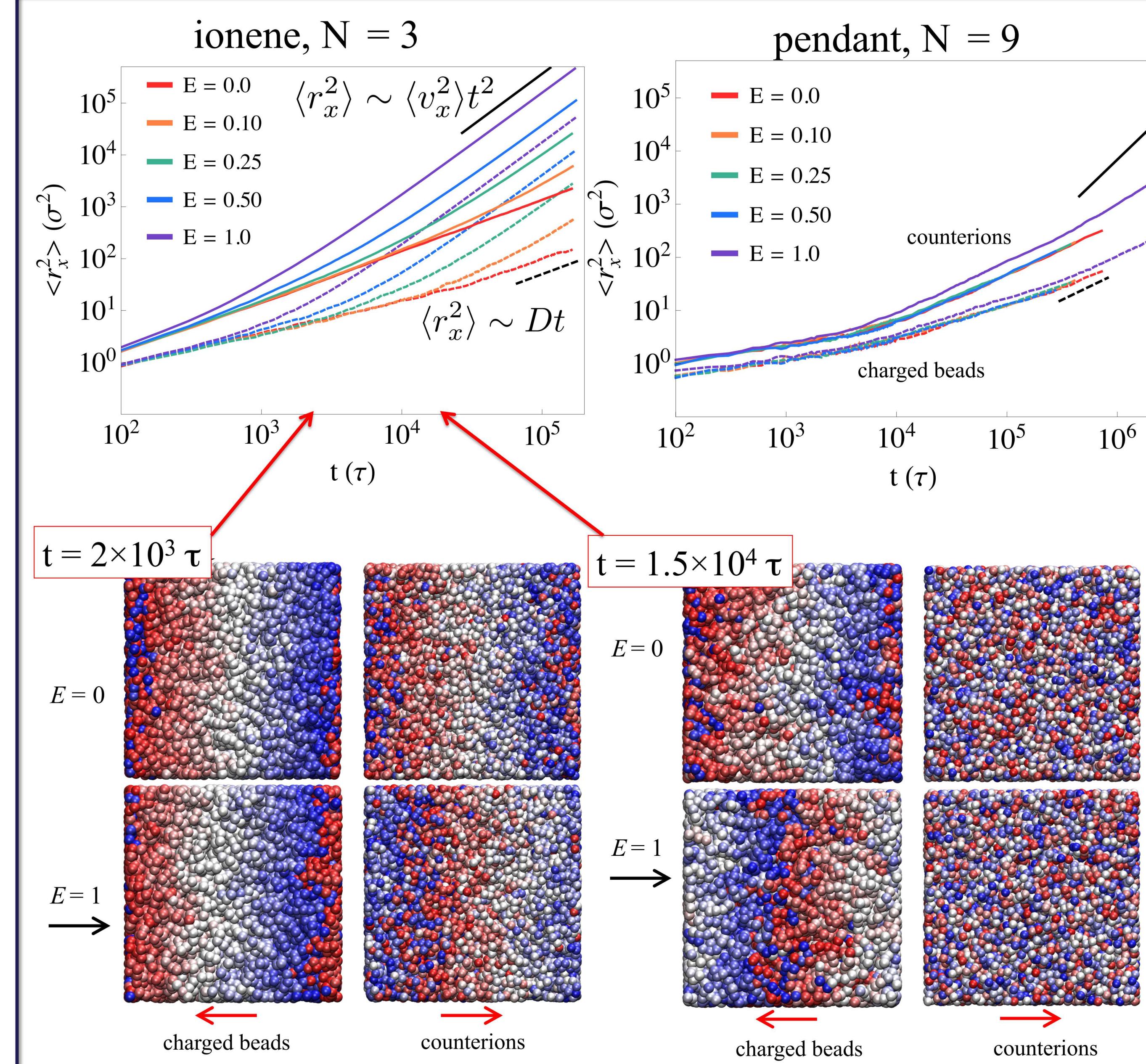
External electric field: adds force $F_x = qE_x$ to each ion

Field effect on aggregate morphologies



- Electrostatic force between two ions at contact is much stronger than force due to the field
- perturbations for $E < 1.0$ are small and do not modify aggregate morphology.

Field effect on Ion dynamics

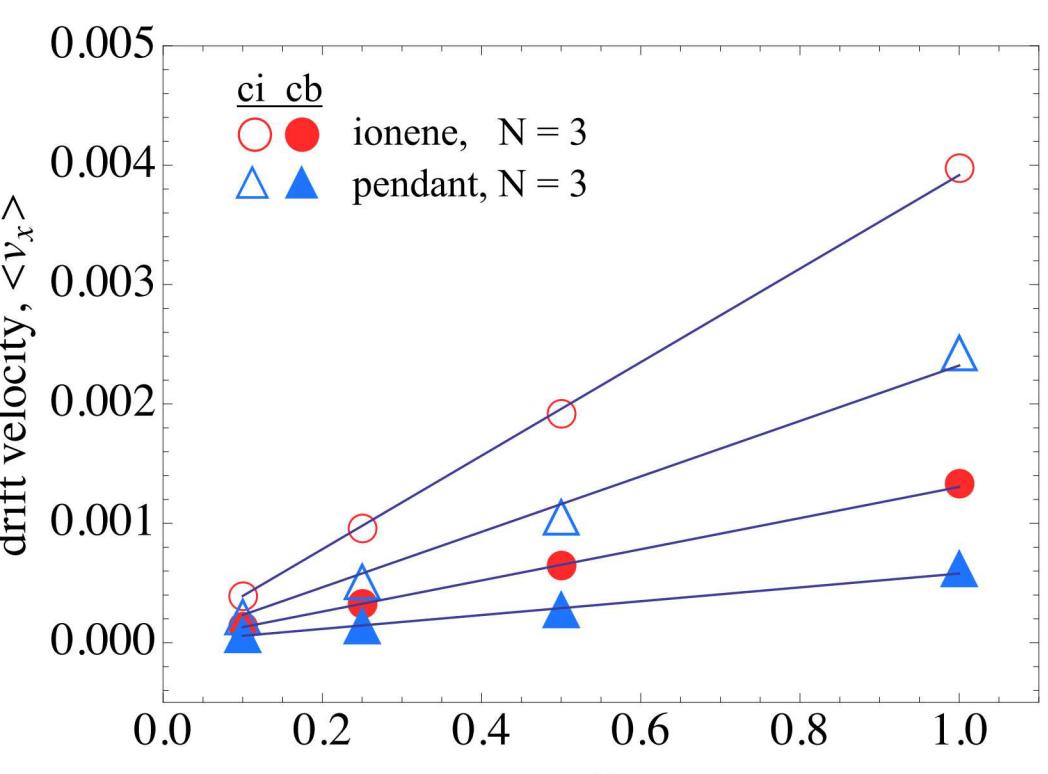


- Field induces transition from Fickian diffusive regime with t scaling to steady state drift regime with t^2 scaling.
- From drift velocities, can extract ion mobilities: $\mu = \langle v_x \rangle / E$
- MSDs of percolated systems increase in a field-dependent manner, but critical field strength required to affect merging and breaking up of isolated aggregates.
- Field does not increase mixing ions separately, but biases drift of ions in opposite directions, speeds up decorrelation of ionic aggregates.

Collective Properties

Conductivity calculated from:

1. Nernst-Einstein (ignores correlations)
2. Collective ionic MSDs
3. Ionic mobilities



ionomer	N	μ_{ci}	μ_{cb}	μ_{ci}/μ_{cb}	λ	$\alpha = \lambda/\lambda^{NE}$
ionene	3	3.92×10^{-3}	1.30×10^{-3}	3.02	5.87×10^{-4}	0.36
pendant	3	2.32×10^{-3}	5.79×10^{-4}	4.01	2.96×10^{-4}	0.40
ionene	7	5.64×10^{-4}	8.23×10^{-5}	6.85	4.72×10^{-5}	0.22
pendant	7	1.43×10^{-4}	1.98×10^{-5}	7.22	1.06×10^{-5}	0.20
ionene	9	3.33×10^{-4}	3.89×10^{-5}	8.56	2.26×10^{-5}	0.18

$$\lambda^{NE} = \rho e^2 (D_{cb} + D_{ci}) \quad \lambda = \rho e (\mu_{ci} - \mu_{cb})$$

- Percolated systems have higher ion mobilities and conductivities
- Ion correlations are significant, but decrease with increasing ion concentrations
- Our model ionomer melts are "subionic". Several reasons why stringy aggregates may not display superionic behavior observed in PEO by Lin and Maranas (PRE, 2013).

Conclusions and Future Work

- Within the linear response regime, the field has no effect on aggregate morphology
- Field speeds up ion motion in percolated system; critical field strength required for discrete aggregates
- Field speeds up decorrelation of aggregates by basing ions in opposite directions
- Ion motions are correlated; systems are "subionic"
- High conductivities related to percolated systems with high ion concentrations.
- Apply oscillating electric fields to make comparisons with dielectric relaxation spectroscopy (DRS) experiments

C. L. Ting, M. J. Stevens, and A. L. Frischknecht, manuscript in preparation