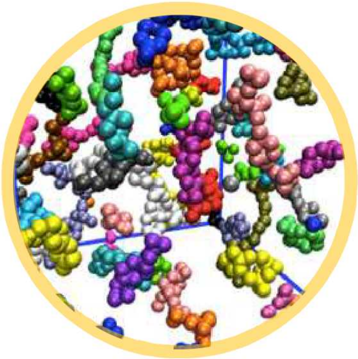
SAND2019-14537C

Aggregate dynamics in ionomer melts: ion transport in networks versus clusters

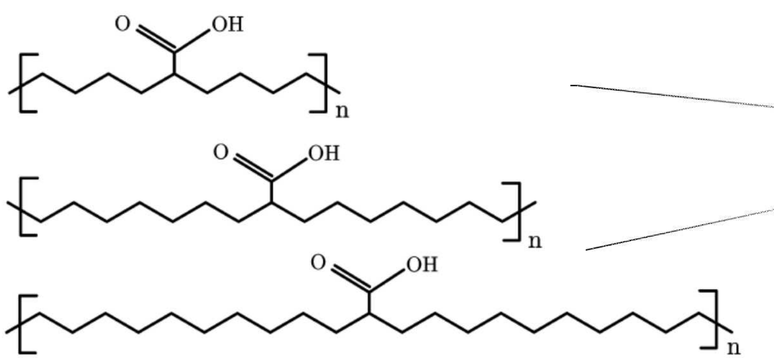


Jonathan A. Bollinger, Mark J. Stevens, and Amalie L. Frischknecht

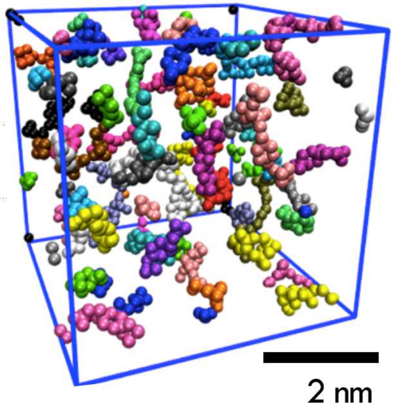
Center for Integrated Nanotechnologies
Sandia National Laboratories
March 8, 2018

This work was performed, in part, at the Center for Integrated Nanotechnologies, an Office of Science User Facility operated for the U.S. Department of Energy (DOE) Office of Science. Sandia National Laboratories is a multi-mission laboratory managed and operated by National Technology and Engineering Solutions of Sandia, LLC., a wholly owned subsidiary of Honeywell International, Inc., for the U.S. Department of Energy's National Nuclear Security Administration under contract DE-NA0003525.

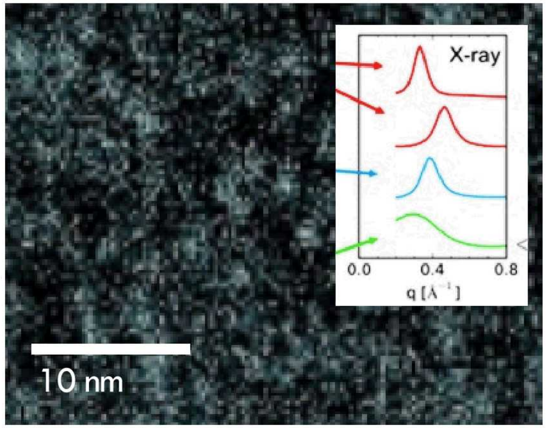
Ionomers are “designer” conductive polymers



Ionomer chemical structures for various precise spacings (Bolintineanu 2013)



Atomistic simulation of dense melt, showing charged species only (Bolintineanu 2013)



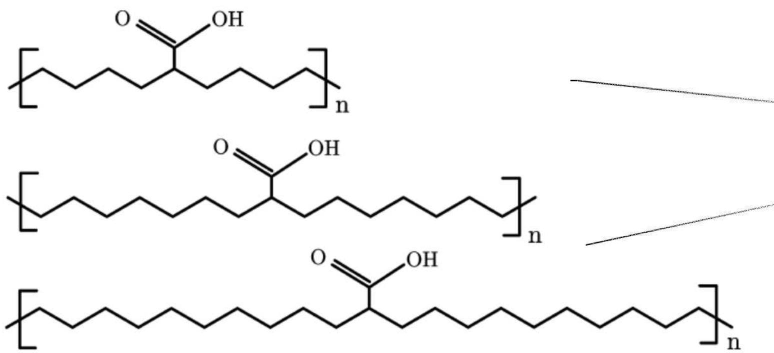
Dark-field STEM and SAXS (inset) of charged species (Middleton 2017, Trigg 2017)

Polymers with (evenly-)spaced charged-groups—can drive formation of ion **aggregates** in melts

Conductivity plus durability makes ionomers candidate **battery materials**

Bolintineanu, et al. ACS Macro Lett., 2, 2013
Middleton, Winey. Annu. Rev. Chem. Bio. Eng., 8, 2017
Trigg, et. al. ACS Macro Lett., 6, 2017

Ionomers are "designer" conductive polymers



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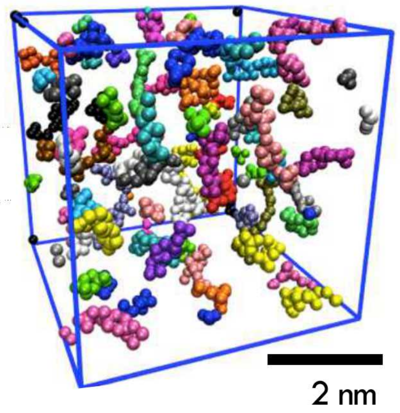

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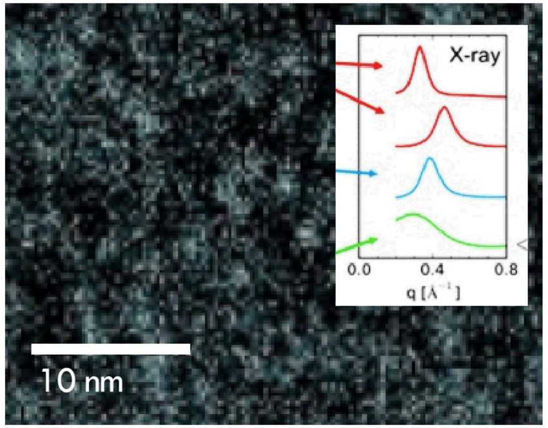


Dark-field STEM and SAXS (inset) of charged species (Middleton 2017, Trigg 2017)

Goals

Identify polymer architectures that promote rapid ion transport

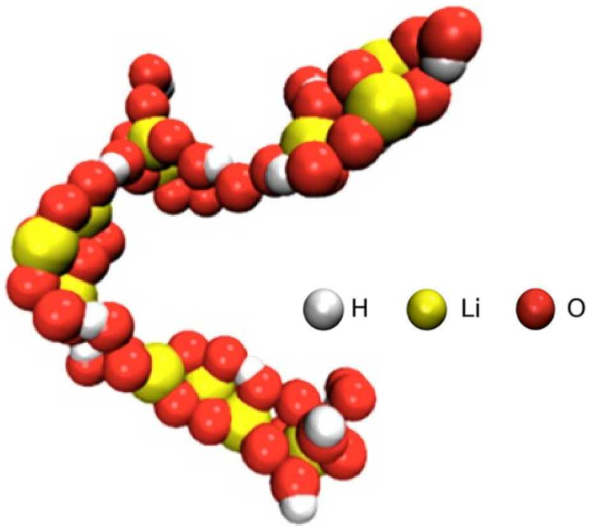
Connect transport mechanisms to underlying aggregation structure

↳ **Coarse-grained model** to simulate morphology and dynamics

Bolintineanu, et al. ACS Macro Lett., 2, 2013
Middleton, Winey. Annu. Rev. Chem. Bio. Eng., 8, 2017
Trigg, et. al. ACS Macro Lett., 6, 2017

Charged species aggregate due to competing interactions

short-range attraction



strong electrostatic contact energy
drives aggregation

Bolintineanu, et al. ACS Macro Lett., 2, 2013.

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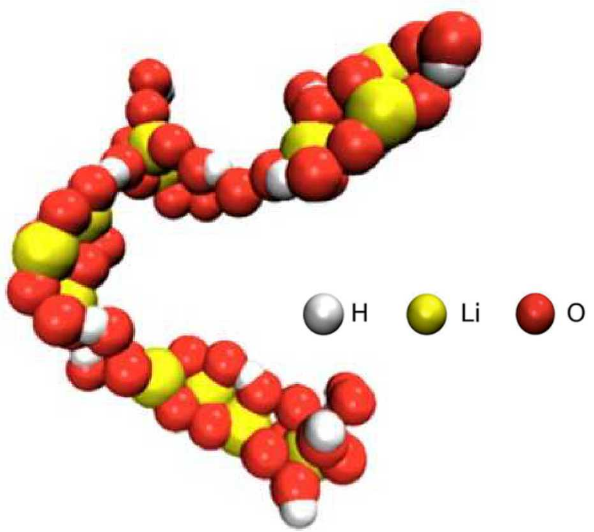

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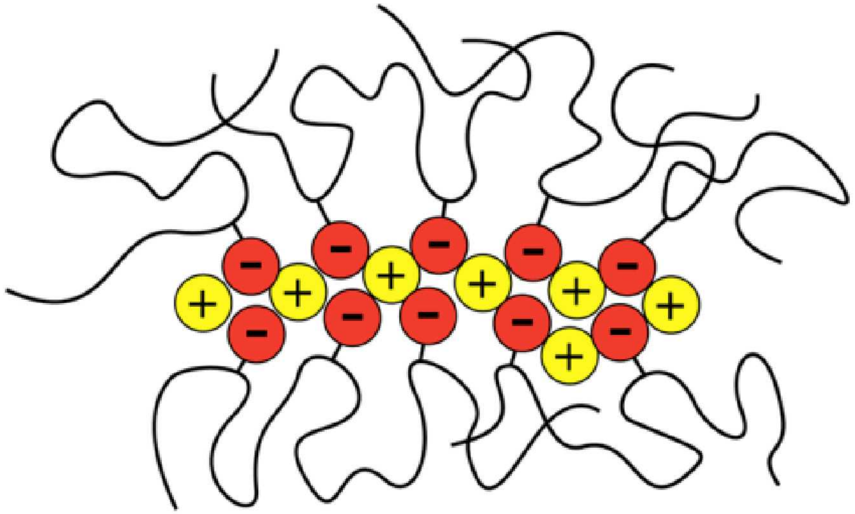
steric repulsion



polymer backbone packing
halts aggregation

Bolintineanu, et al. ACS Macro Lett., 2, 2013.

Charged species aggregate due to competing interactions

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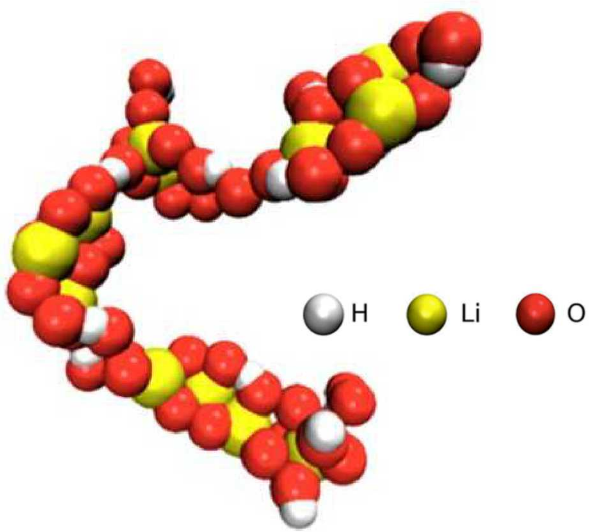

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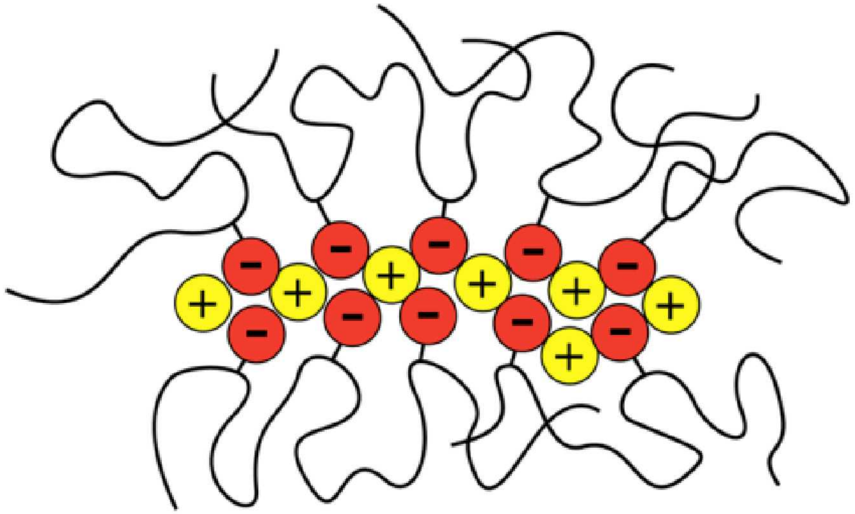
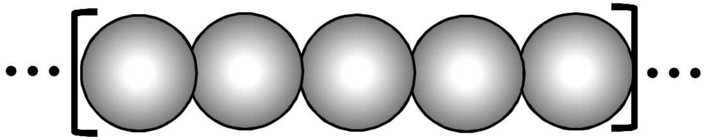


Balancing these interactions drives formation of charged-species morphologies with **finite characteristic sizes**

Bolintineanu, et al. ACS Macro Lett., 2, 2013.

Coarse-grained model for ionomer melts



Fully-flexible backbone (Kremer-Grest model)

Purely repulsive beads, size ≡ 1σ – each maps to 3 to 4 CH_2 units

Hall, et. al. PRL, 106, 2011; Hall, et. al. JACS, 134, 2012; Hall, et. al. Macromolecules, 45, 2012.

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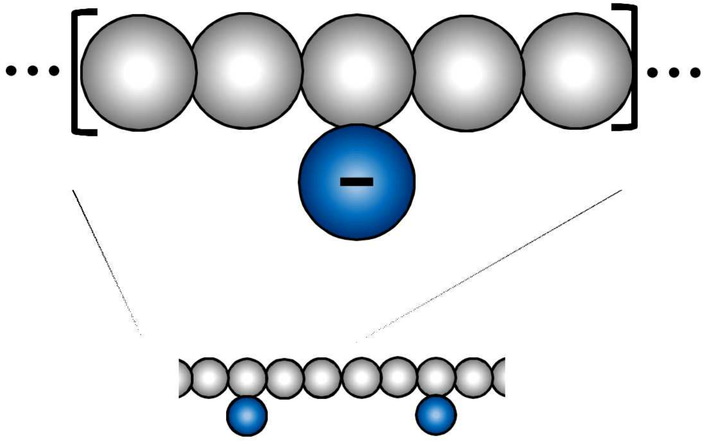

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Precisely-spaced pendant anionic groups (z=-1)

Purely-repulsive beads plus charge, size ≡ 1σ – maps to COO^-

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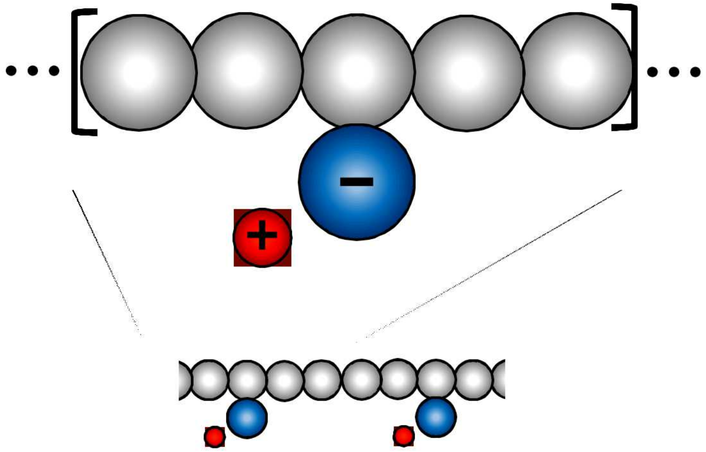

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Fully neutralized by cationic counterions (z=+1)

Purely-repulsive beads plus charge, size $\equiv 0.5\sigma$ – maps to Na+

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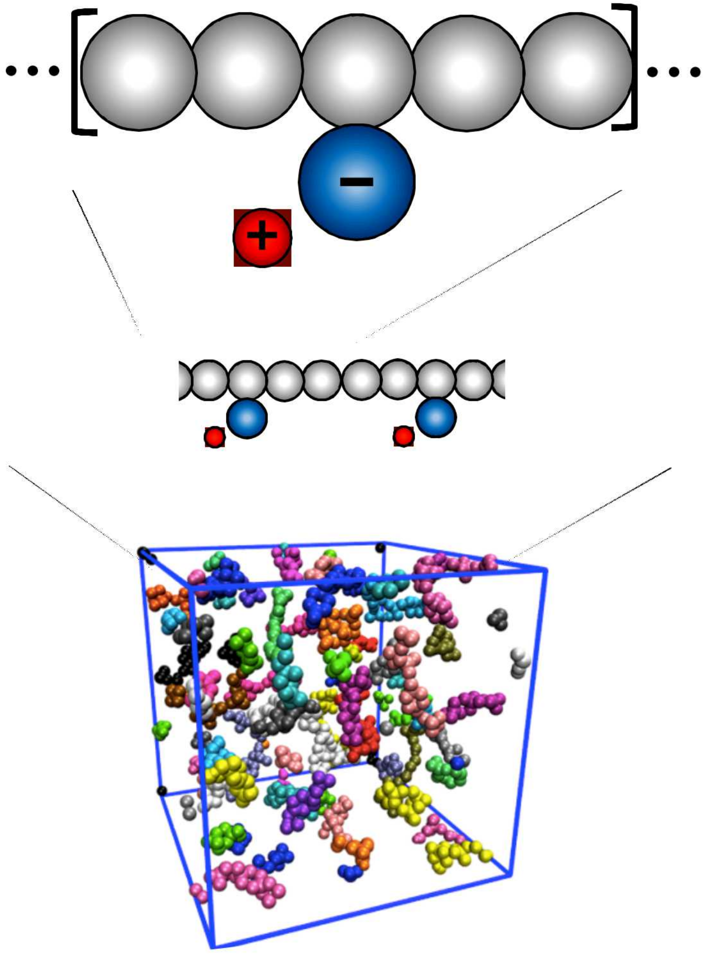
Coarse-grained model for ionomer melts



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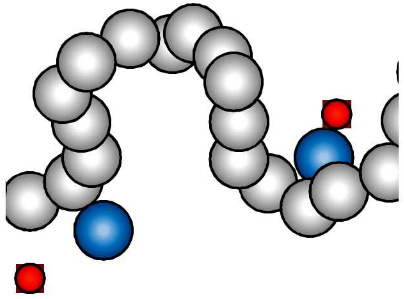
Dense disordered melts of 800 polymers

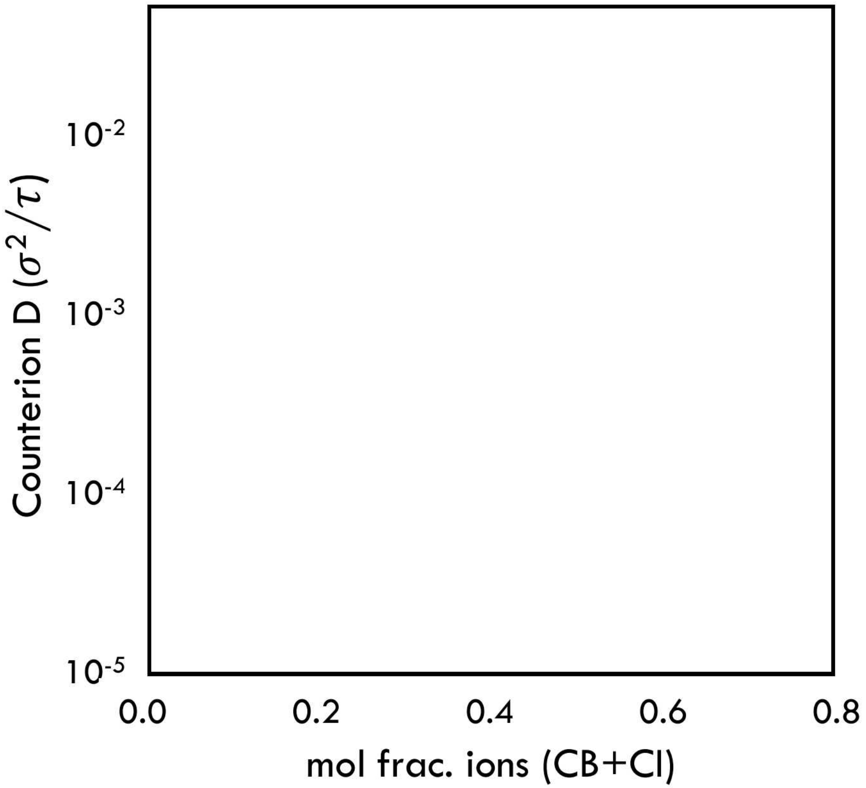
Molecular dynamics (Langevin thermostat) via LAMMPS

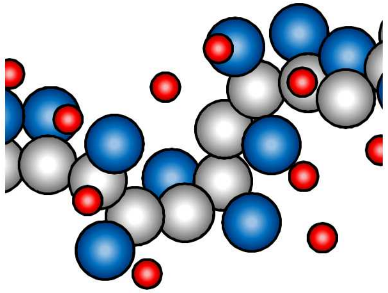
Hall, et. al. PRL, 106, 2011; Hall, et. al. JACS, 134, 2012; Hall, et. al. Macromolecules, 45, 2012.

1) Dependence of counterion dynamics on polymer architecture?

p13 polymer (sparse)







p1 polymer (“polyIL”)

From large spacer lengths to the “polymeric ionic liquid” limit—

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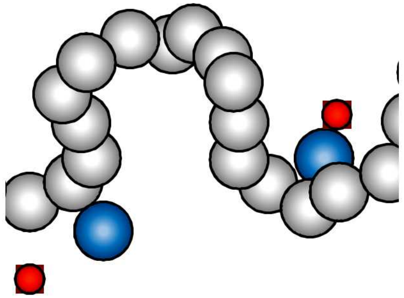

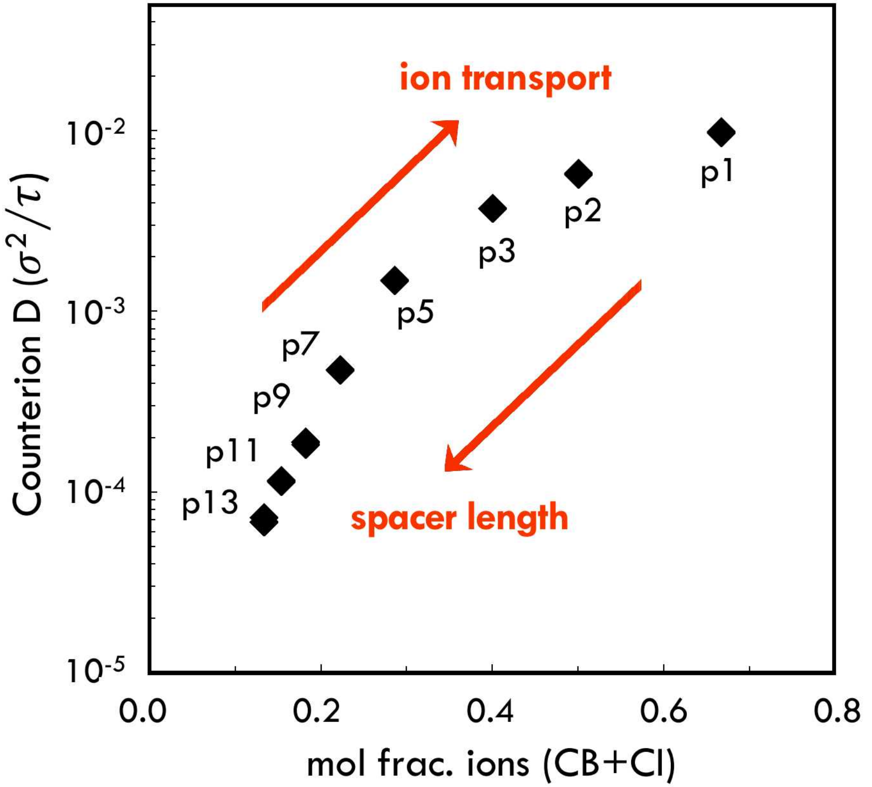

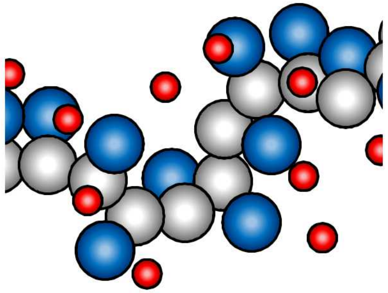

p1 polymer ("polyIL")

From large spacer lengths to the "polymeric ionic liquid" limit—

negative correlation between D_{CI} and ionic content

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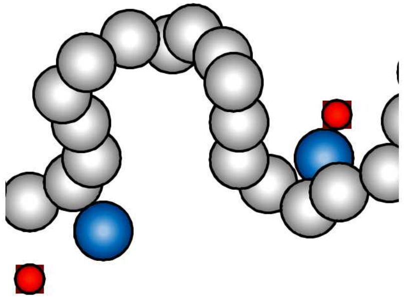
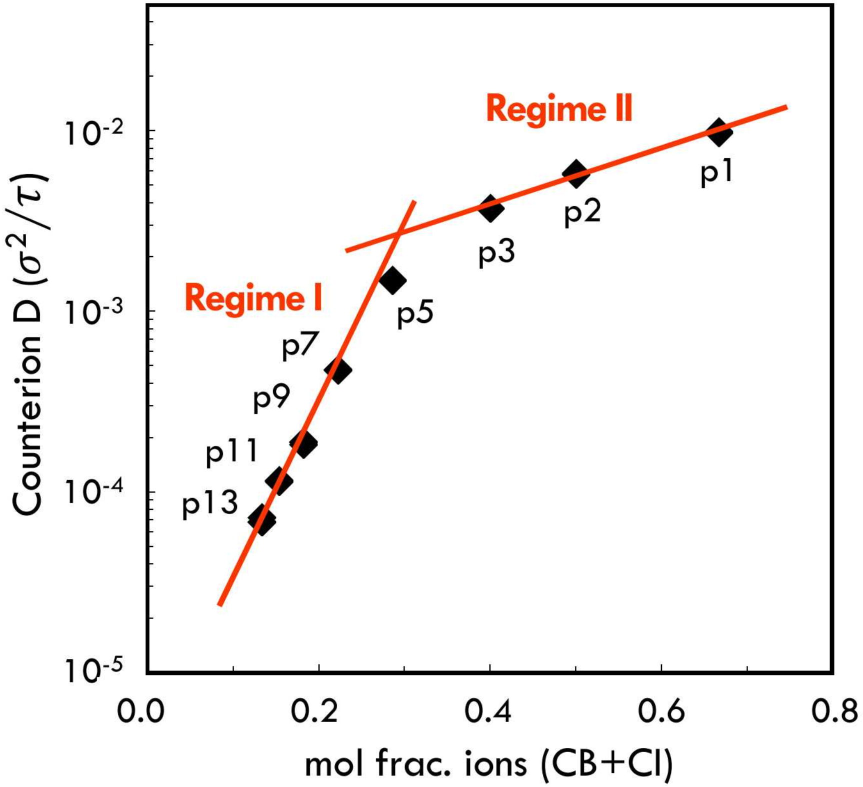
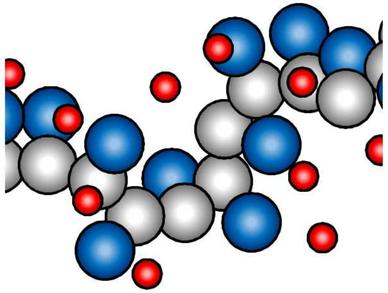




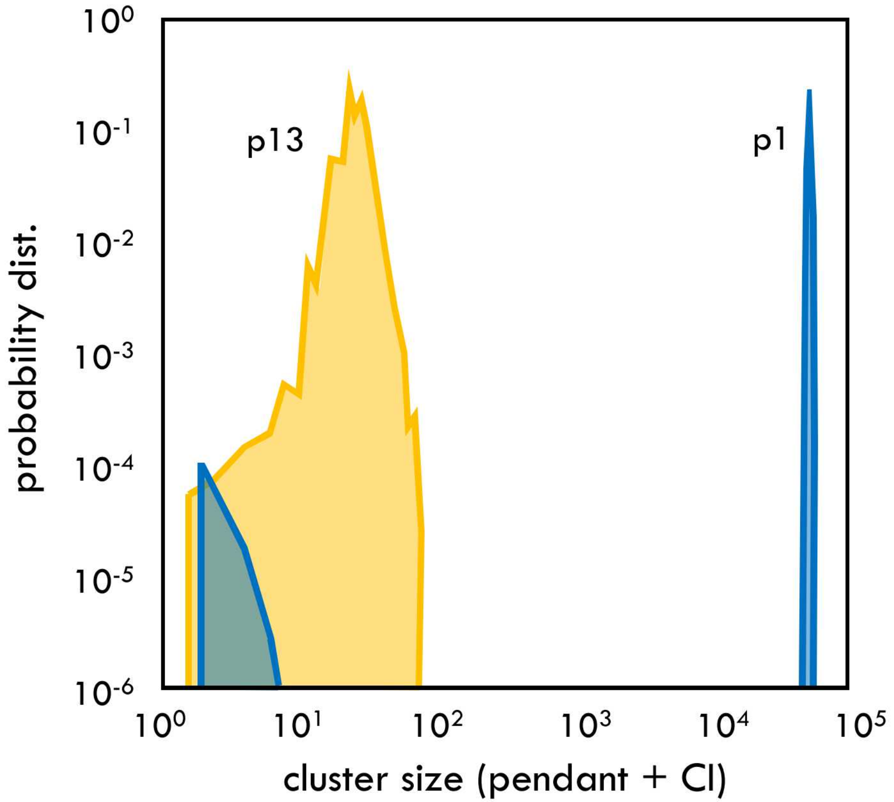


p1 polymer ("polyIL")

From large spacer lengths to the "polymeric ionic liquid" limit—

two regimes (scaling relns) between D_{Cl} and ionic content

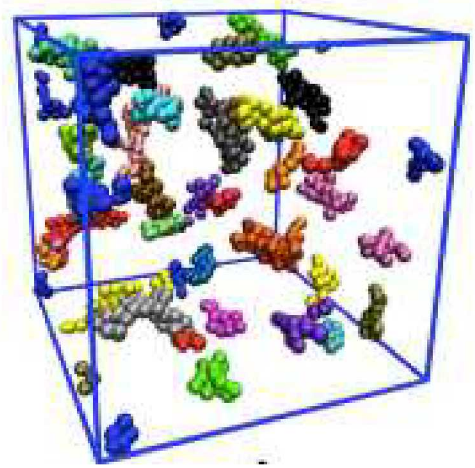
2) Does morphology determine counterion dynamics?

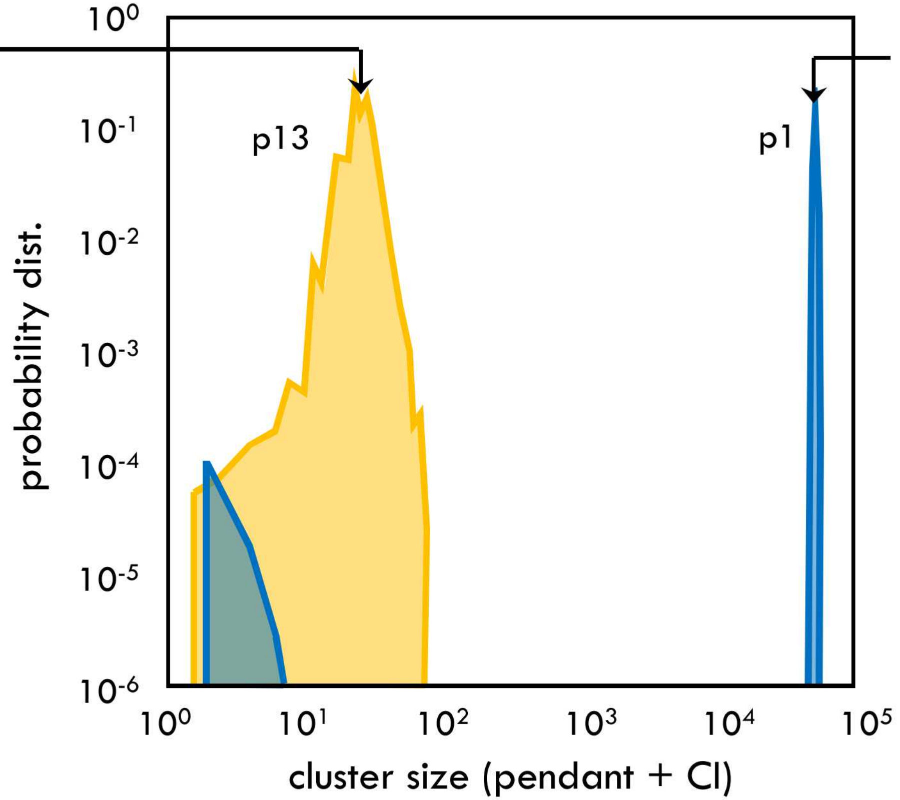


Distinct morphologies observed as a function of spacer length—

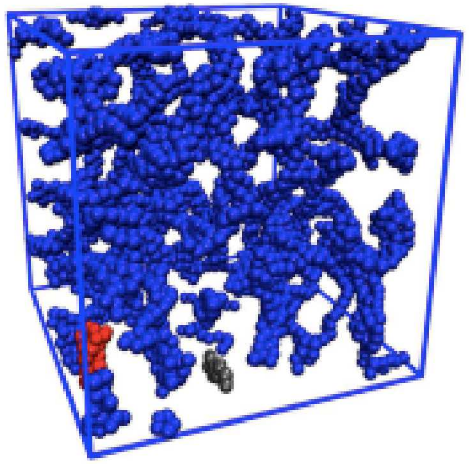
2) Does morphology determine counterion dynamics?

dynamic clusters (N*~30)



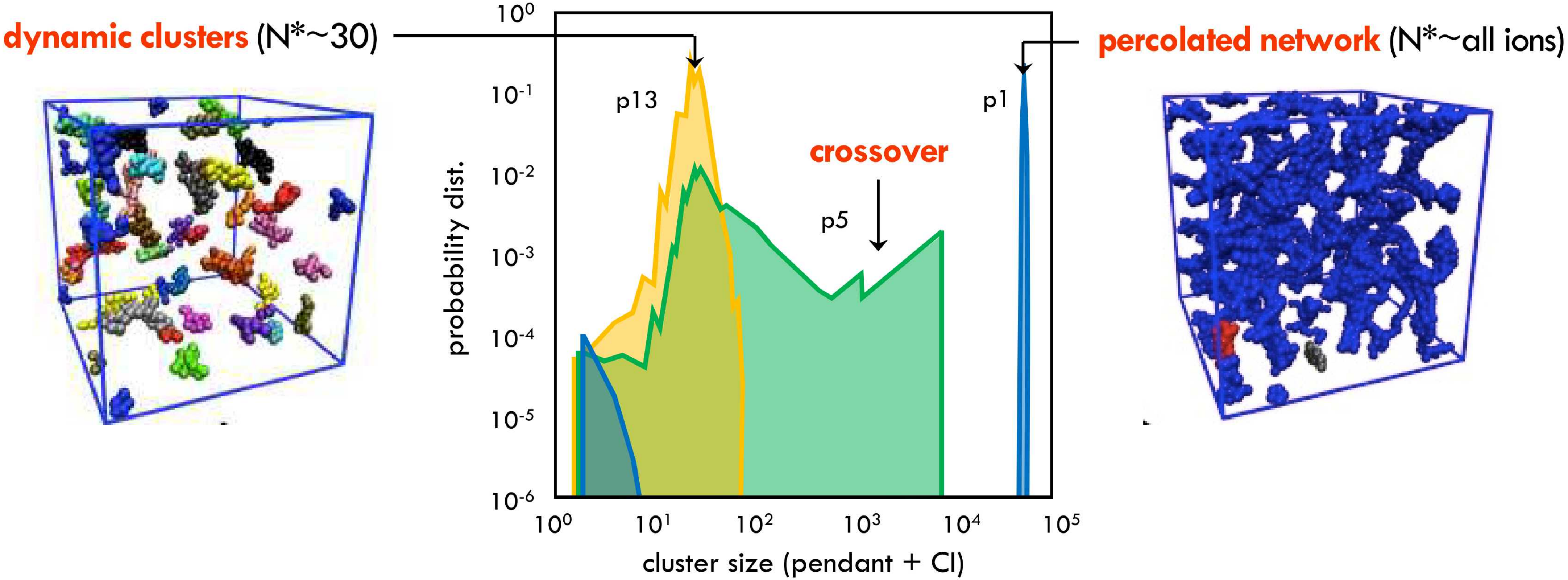


percolated network (N*~all ions)



Distinct morphologies observed as a function of spacer length—
from self-limiting **clusters** to **percolating networks**

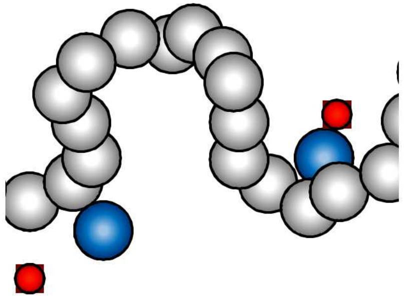
2) Does morphology determine counterion dynamics?

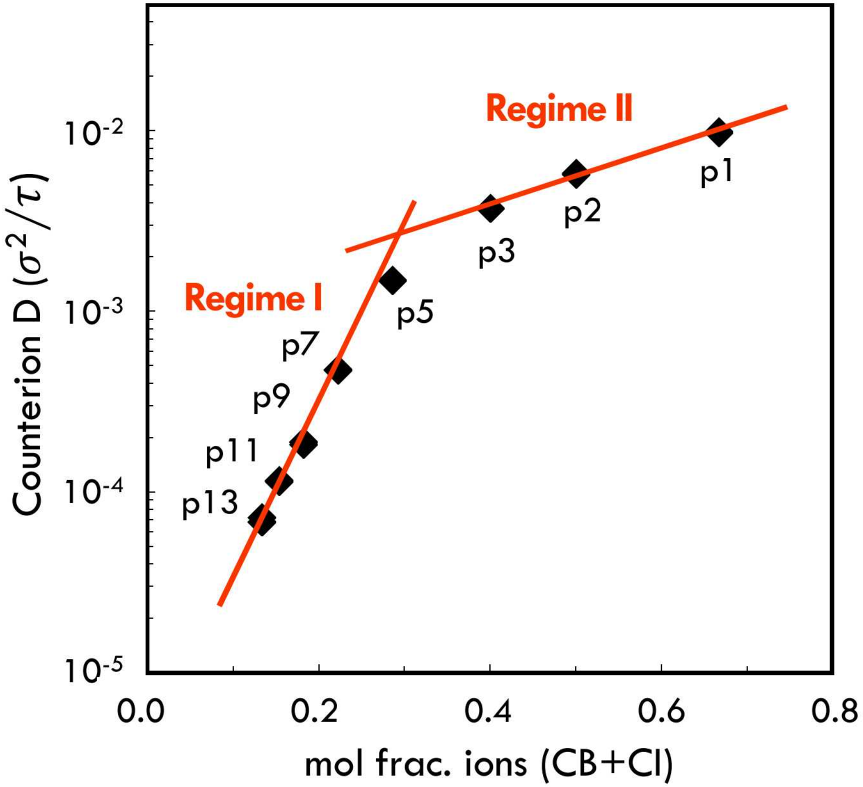


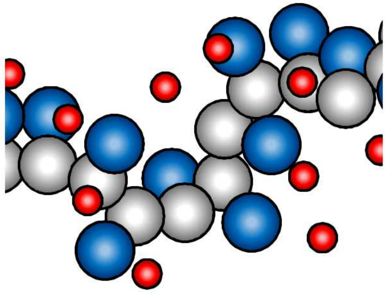
Distinct morphologies observed as a function of spacer length—
including **crossover** region between extremes

2) Does morphology determine counterion dynamics?

p13 polymer (sparse)







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From large spacer lengths to the “polymeric ionic liquid” limit—

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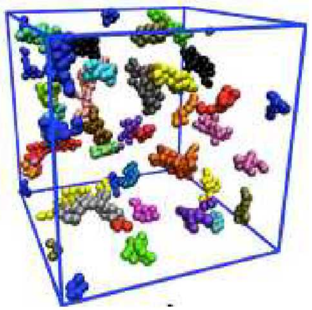

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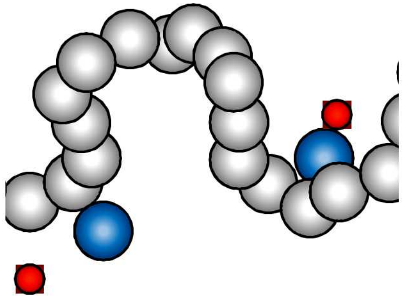

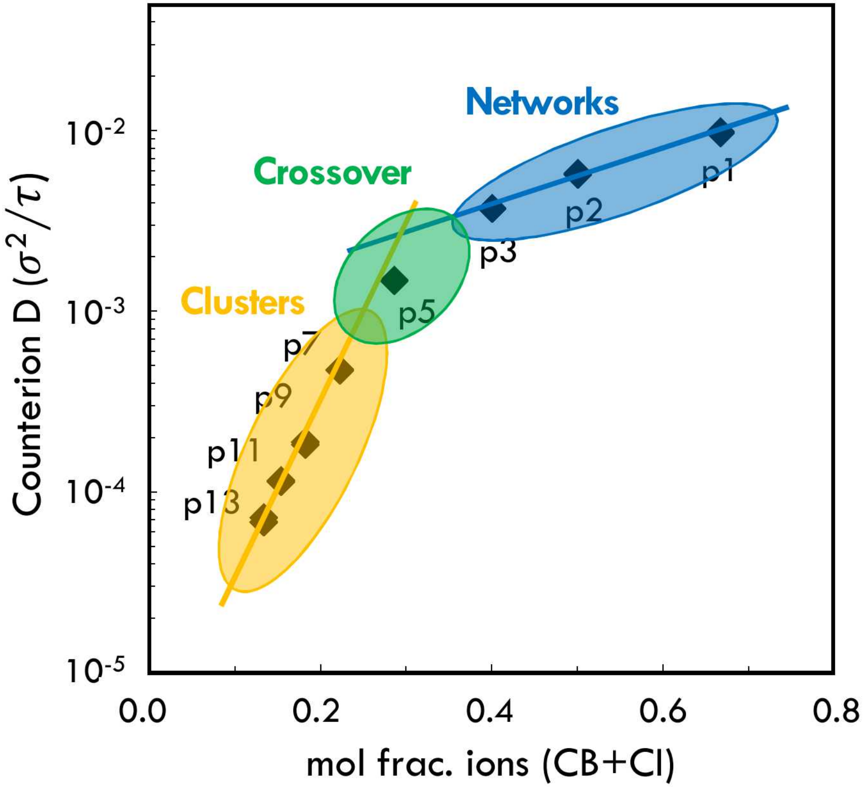

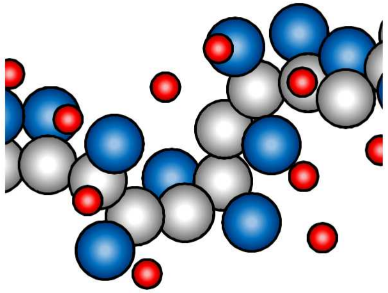

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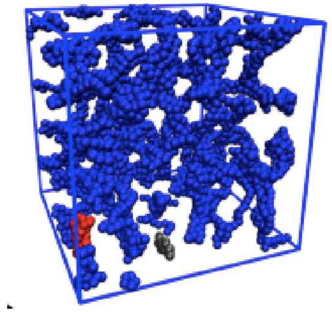
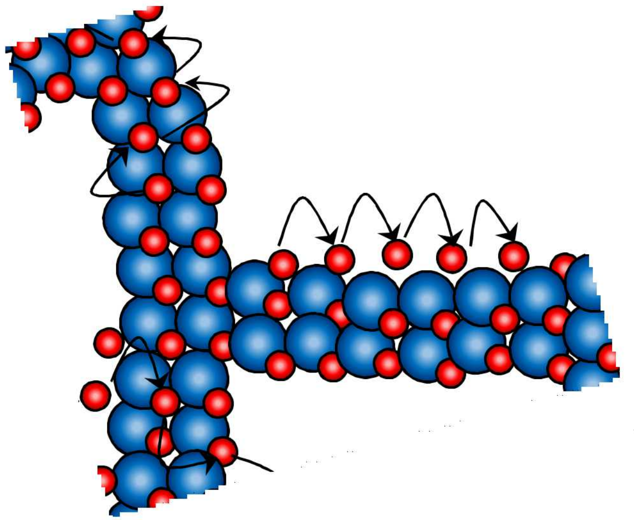


From large spacer lengths to the "polymeric ionic liquid" limit—

two dynamic regimes with two distinct morphologies

3) Physical mechanism(s) by which counterion diffusion occurs?

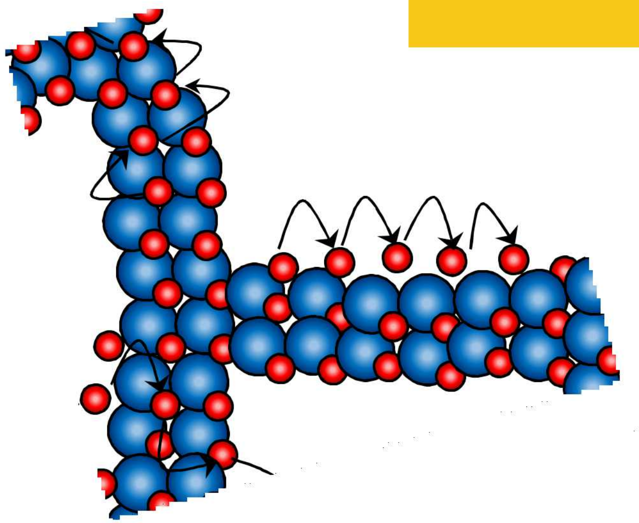


Counterion **stepping** along network "highways" and between cluster "islands"

Mogurampelly, et al. JACS Comm., 139, 2017.

3) Physical mechanism(s) by which counterion diffusion occurs?

Frac. preserved ion-pairs **S(Δt)** $= \dfrac{\langle \#\ \text{ion-pairs preserved thru } \Delta t \rangle}{\langle \#\ \text{ion-pairs} \rangle}$



Counterion stepping along network "highways" and between cluster "islands" quantified by **relative preservation of ion-pair bonds** over time

Mogurampelly, et al. JACS Comm., 139, 2017.

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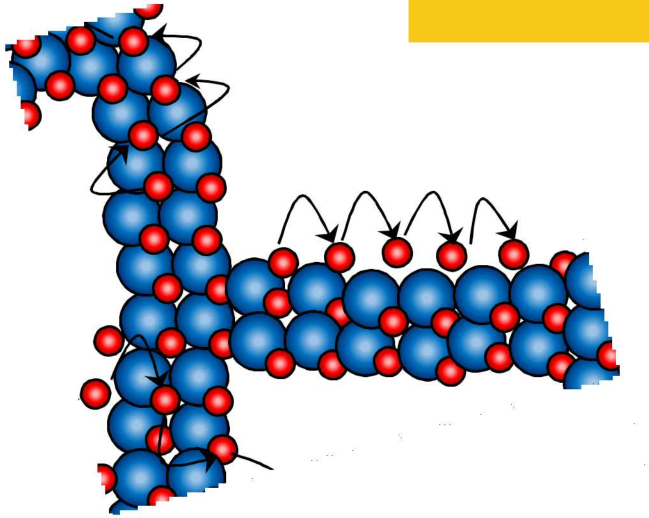

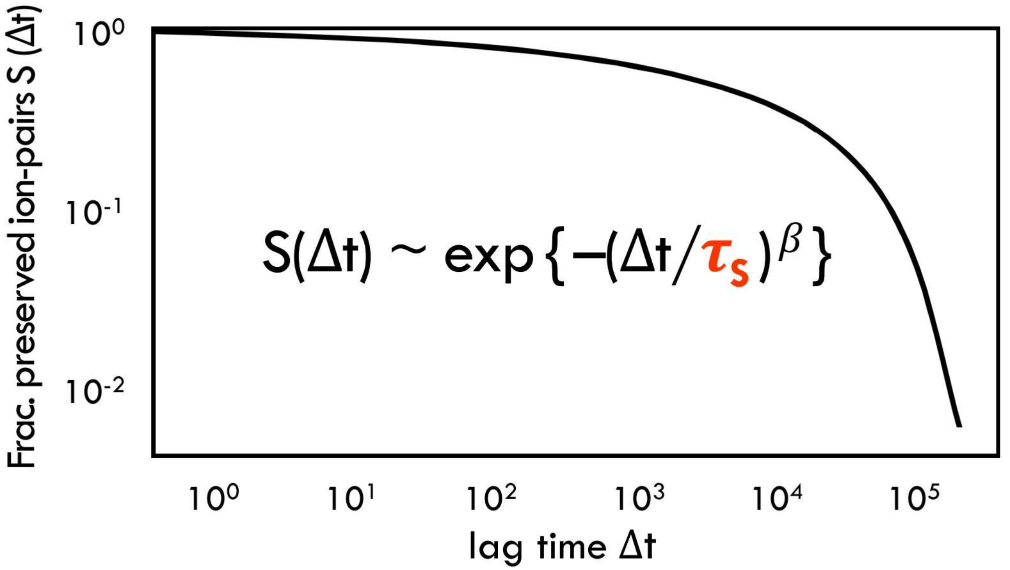

Counterion stepping along network "highways" and between cluster "islands" captured by counterion **stepping timescale τ_s**

Mogurampelly, et al. JACS Comm., 139, 2017.

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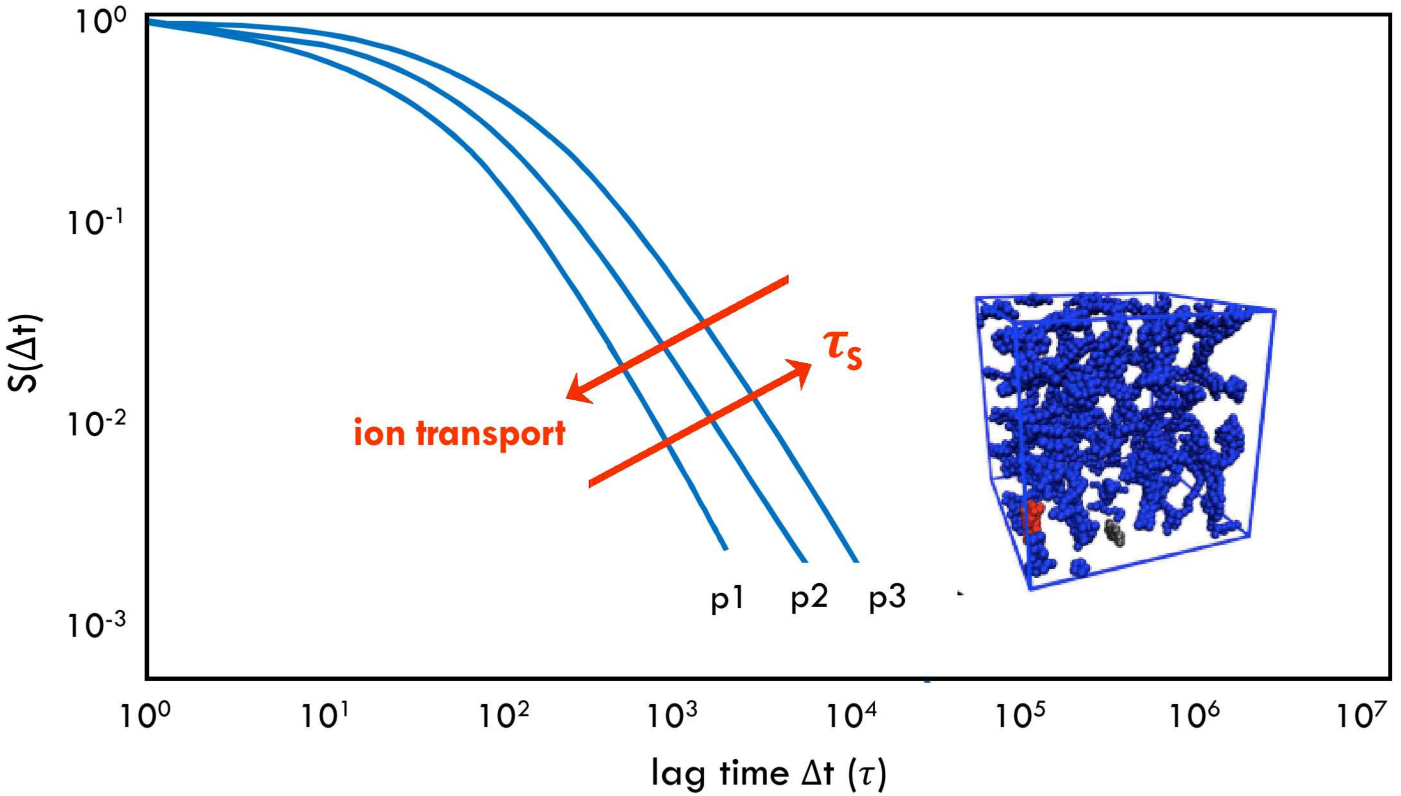

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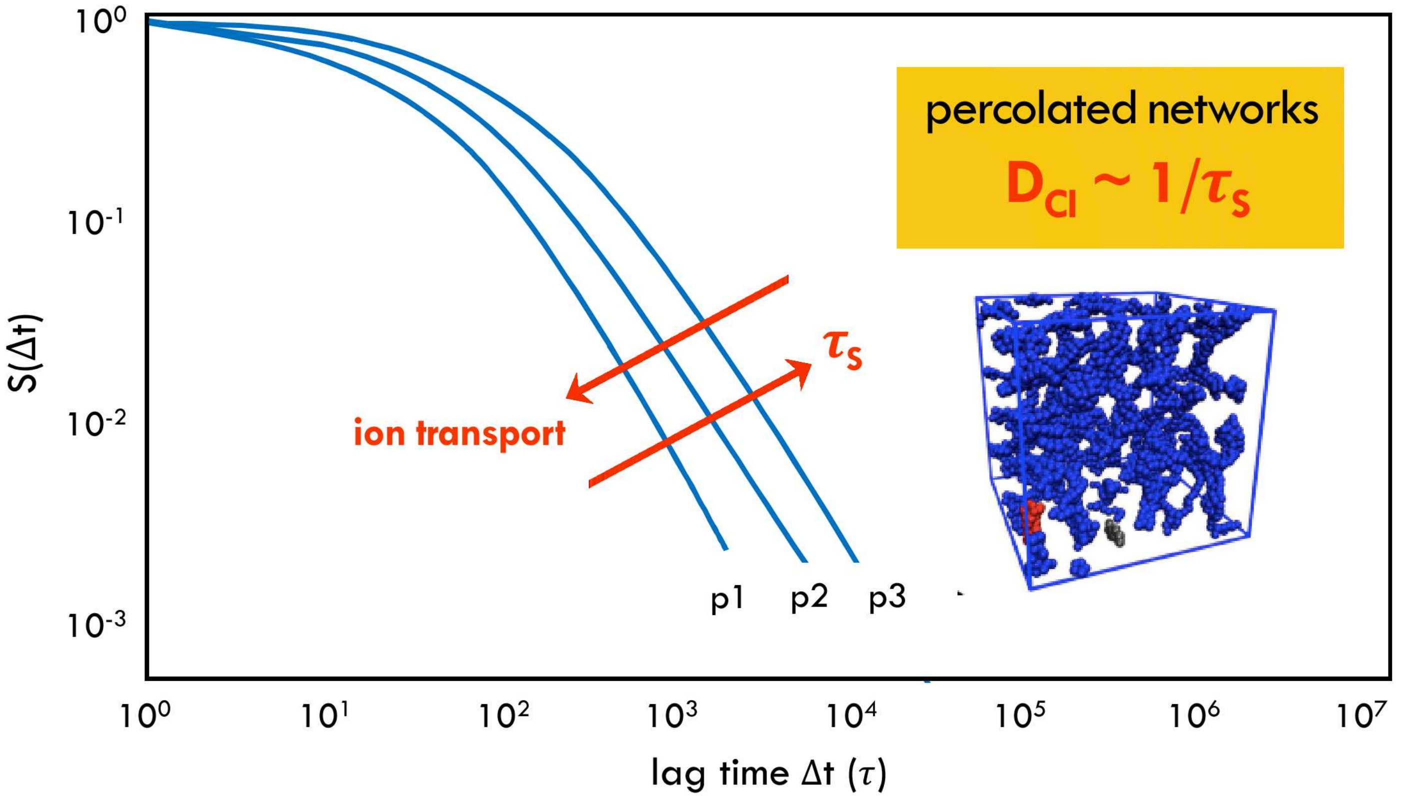

Characteristic stepping timescale τ_s **predicts** ion transport in networks—

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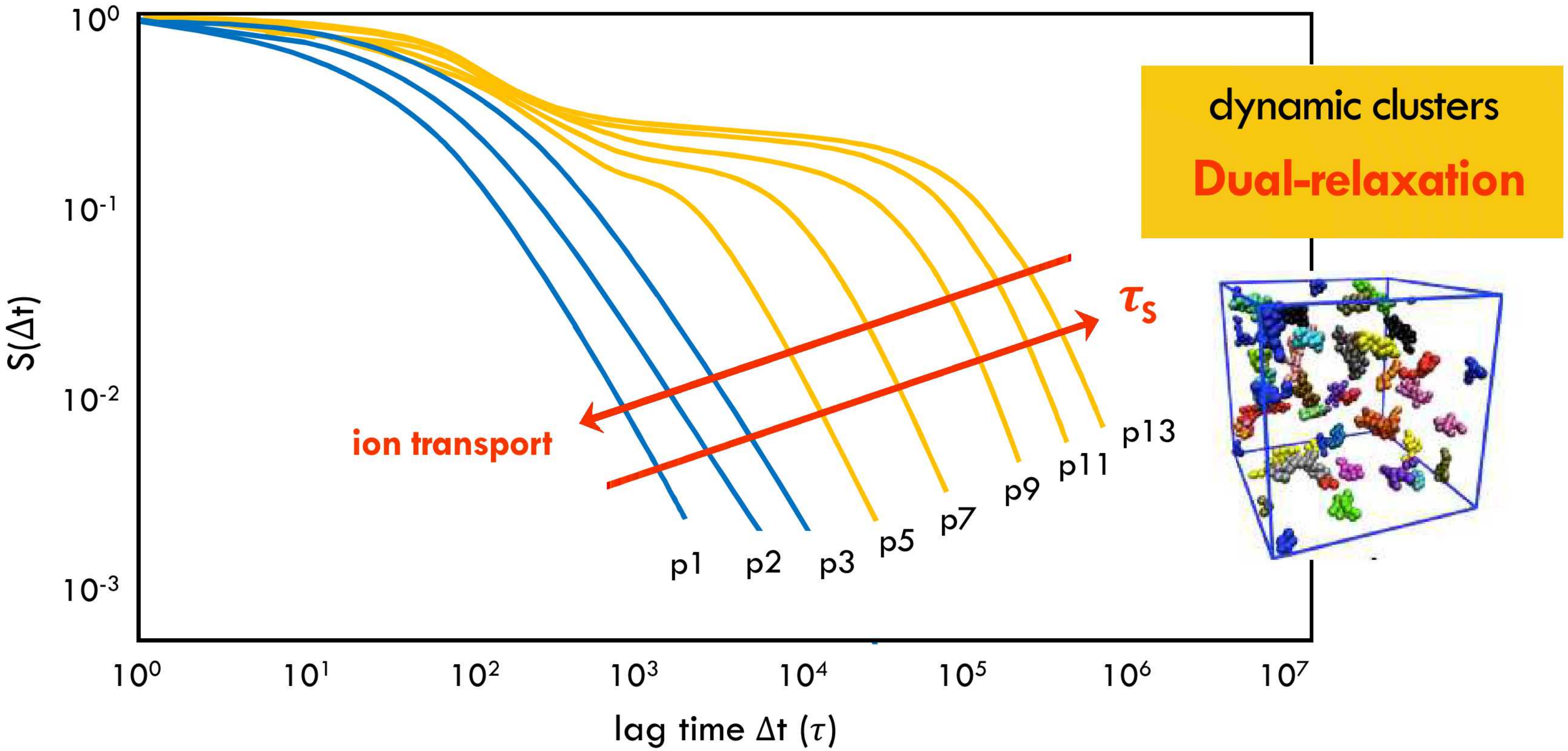
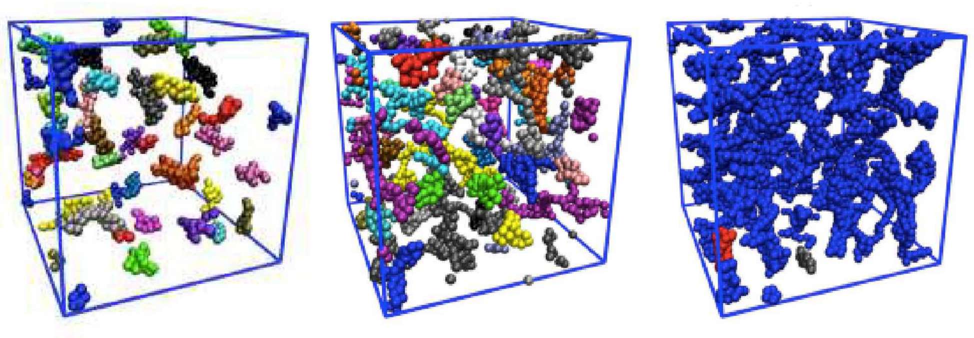


Characteristic stepping timescale τ_S predicts ion transport in networks—

scales **incorrectly** for merge-exchange events between clusters

Concluding remarks

- Described **coarse-grained model** for ionomer melts showing charge aggregation, suitable for examining wide range of diffusive dynamics
- Counterion transport spans **two distinct regimes** as a function of networked versus clustered morphology of ions, where networks exhibit counterion stepping mechanism
- Currently validating best practices for quantifying **"cluster lifetimes" (merge-exchange timescales)** for dynamically clustered systems (relatively ideal test set)



Bolintineanu, et al. ACS Macro Lett., 2, 2013

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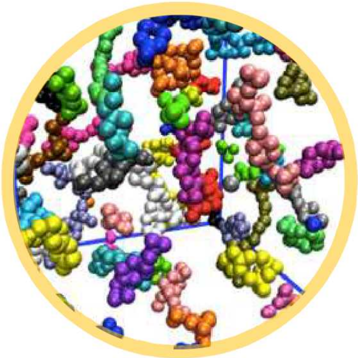

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This research was supported by the U.S. Department of Energy, Office of Basic Energy Sciences, Division of Materials Sciences and Engineering under Award KC0203010. This work was performed, in part, at the Center for Integrated Nanotechnologies, an Office of Science User Facility operated for the U.S. Department of Energy (DOE) Office of Science. Sandia National Laboratories is a multi-mission laboratory managed and operated by National Technology and Engineering Solutions of Sandia, LLC., a wholly owned subsidiary of Honeywell International, Inc., for the U.S. Department of Energy's National Nuclear Security Administration under contract DE-NA0003525.

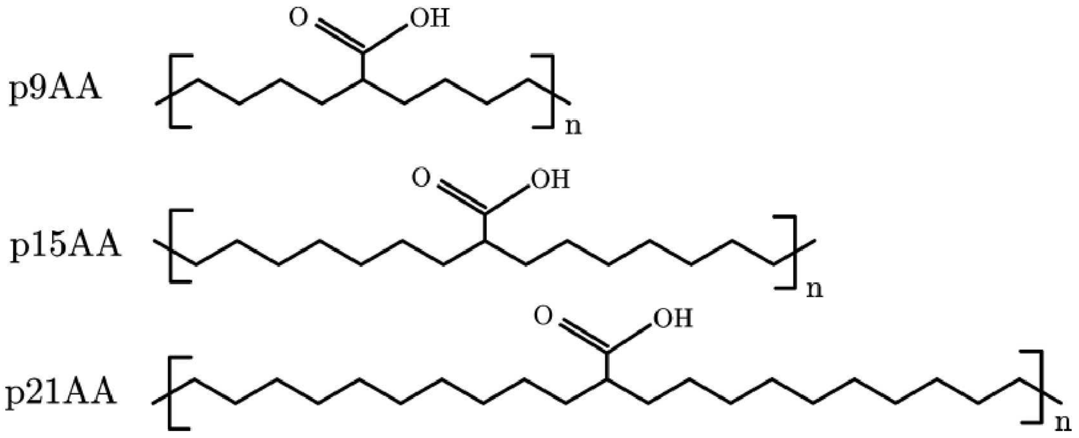
Controllable synthesis parameters in experiments

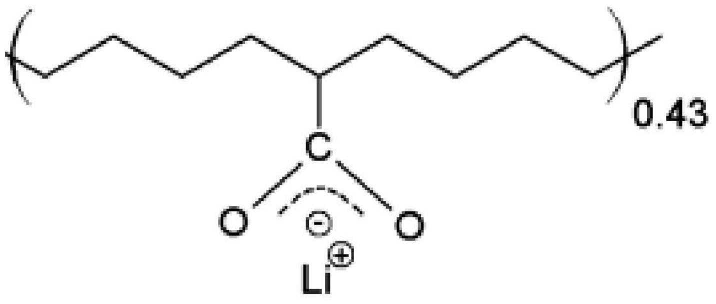
pX – average backbone spacer length (no. of carbons)

p/np/r – charged-group integration: precise, nearly-precise, random

Na+ – counterion species: Na,Li,Zn,Cs

%Na – neutralization level: 20,30,40,50...100%





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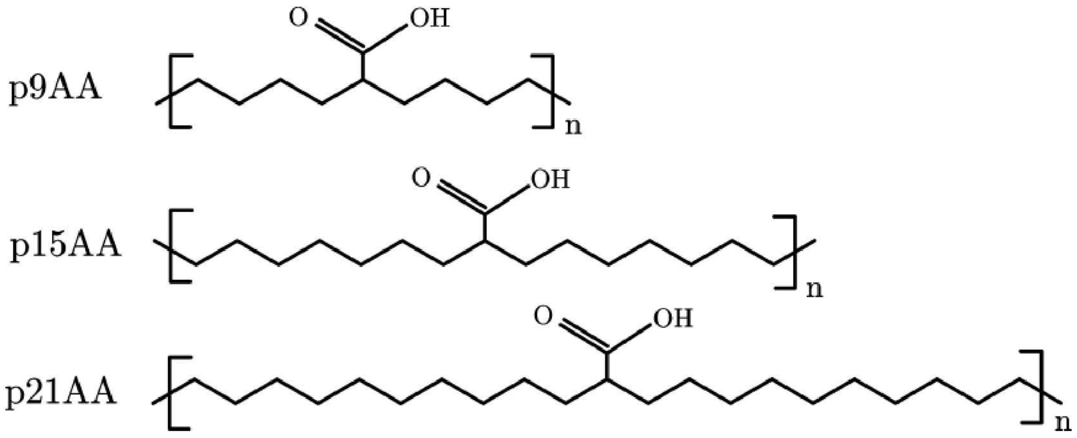

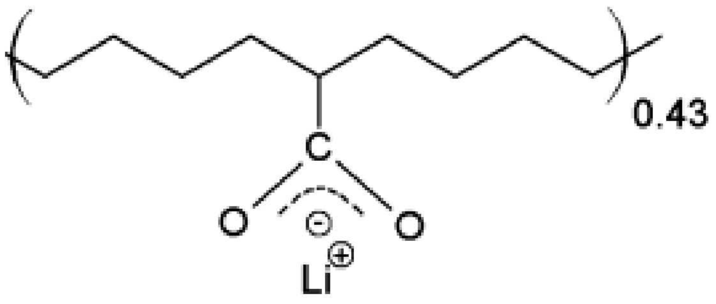

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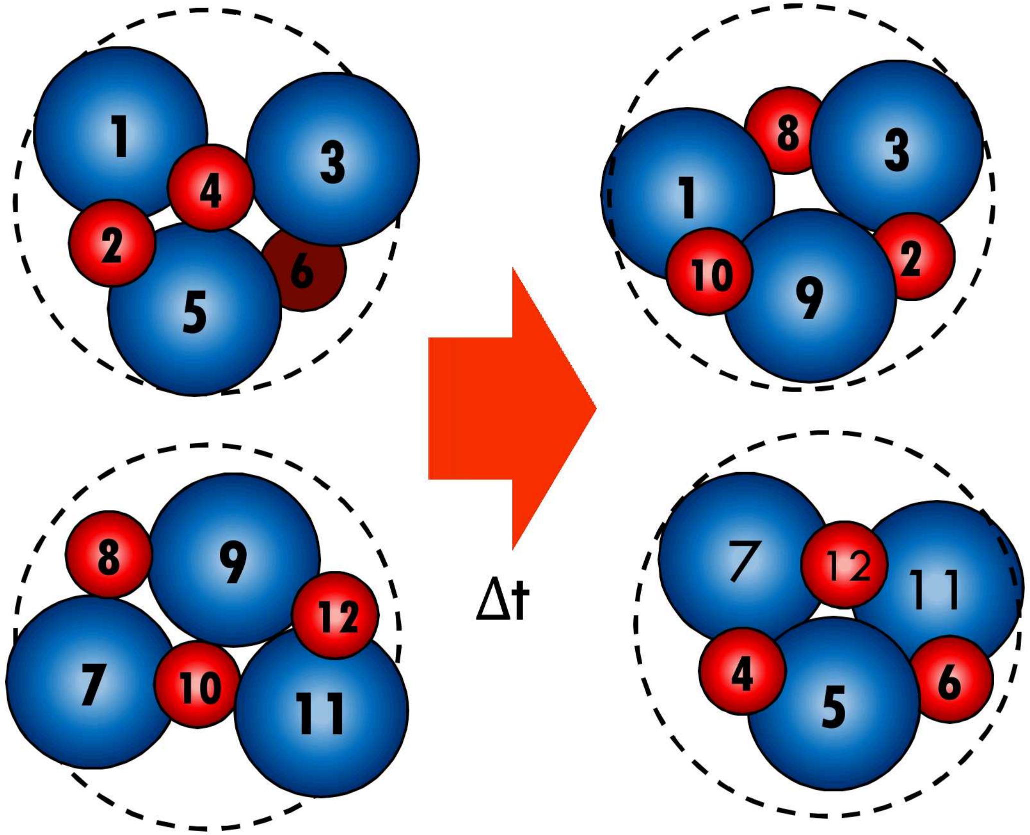
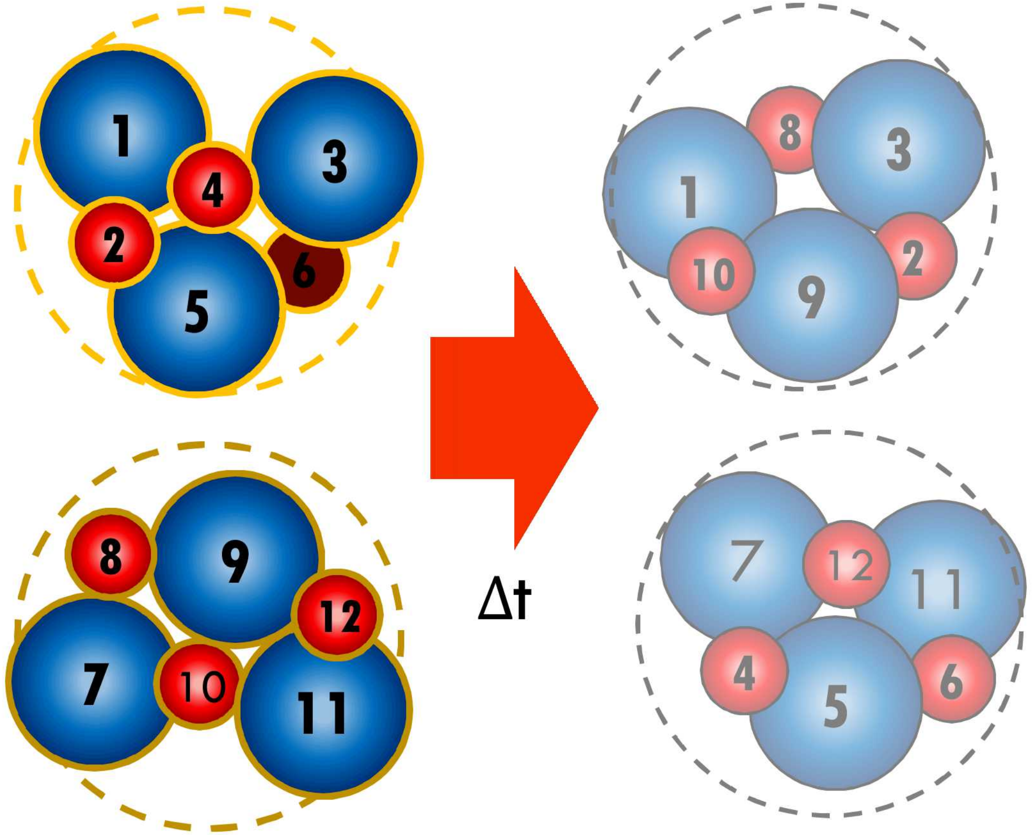
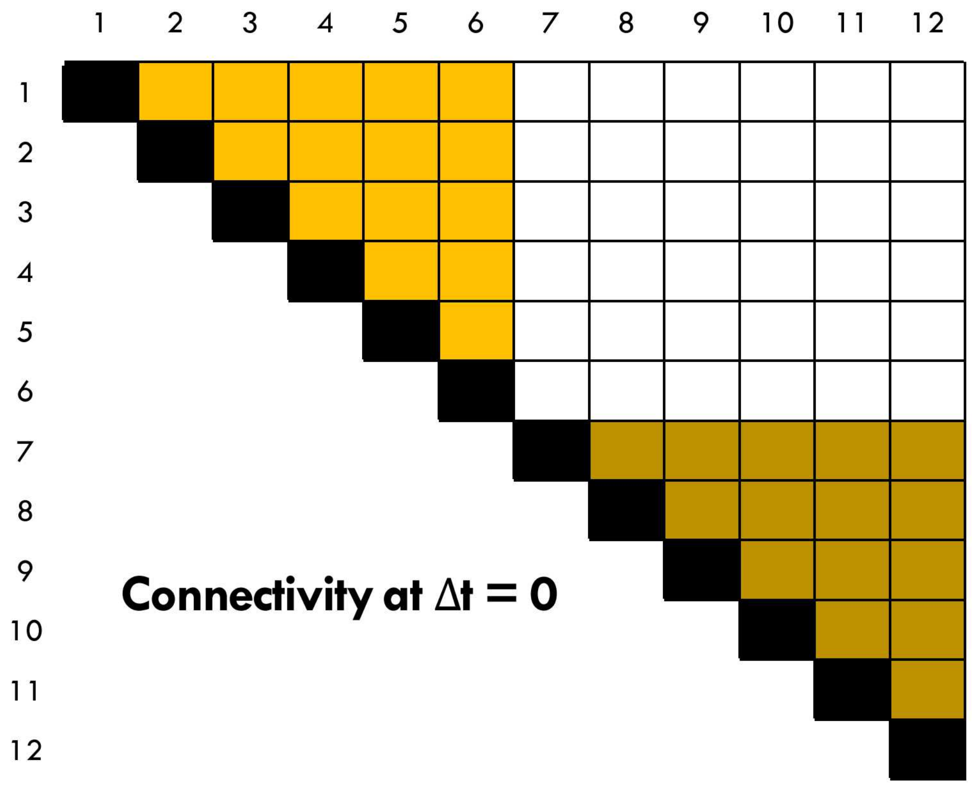


Counterion diffusion via merge-exchange events between clusters—

"cluster lifetimes" more salient than bond lifetimes?

3) Physical mechanism(s) by which counterion diffusion occurs?

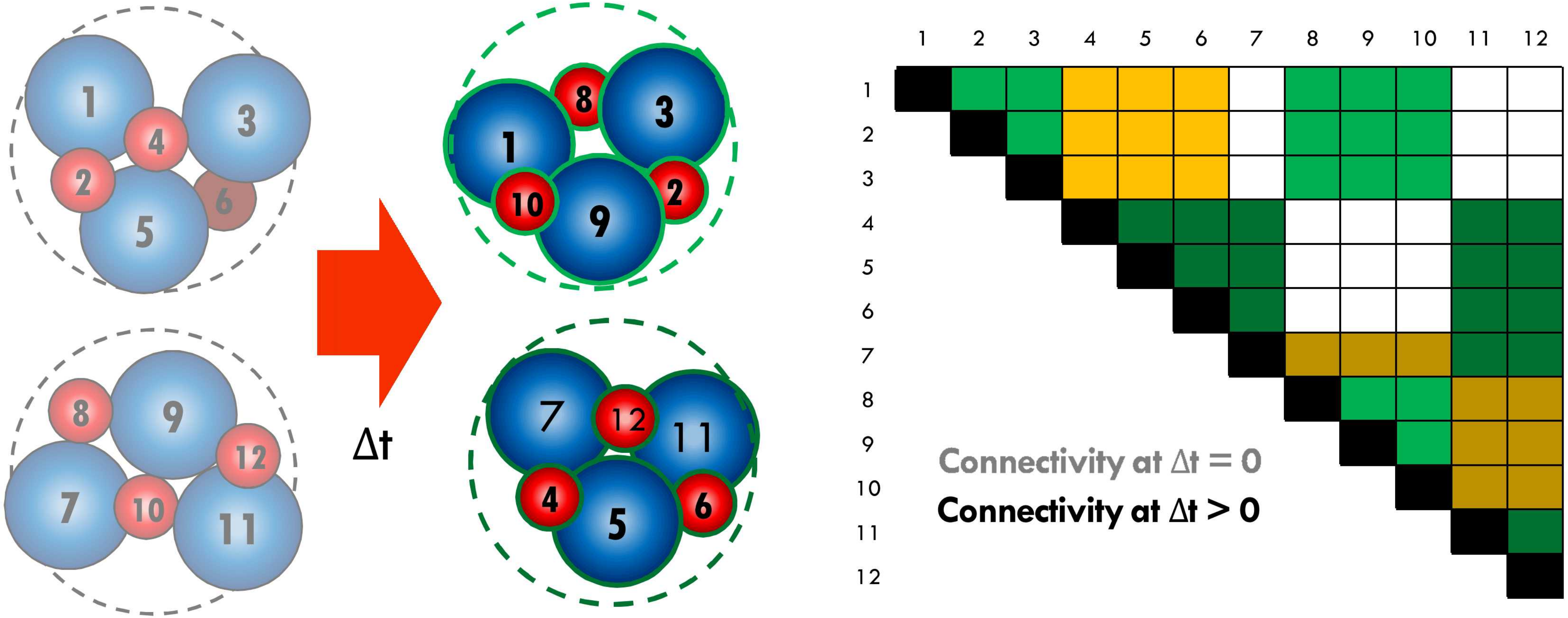




Counterion diffusion via merge-exchange events between clusters—

consider **shared connectivity (similarity)** over time

3) Physical mechanism(s) by which counterion diffusion occurs?



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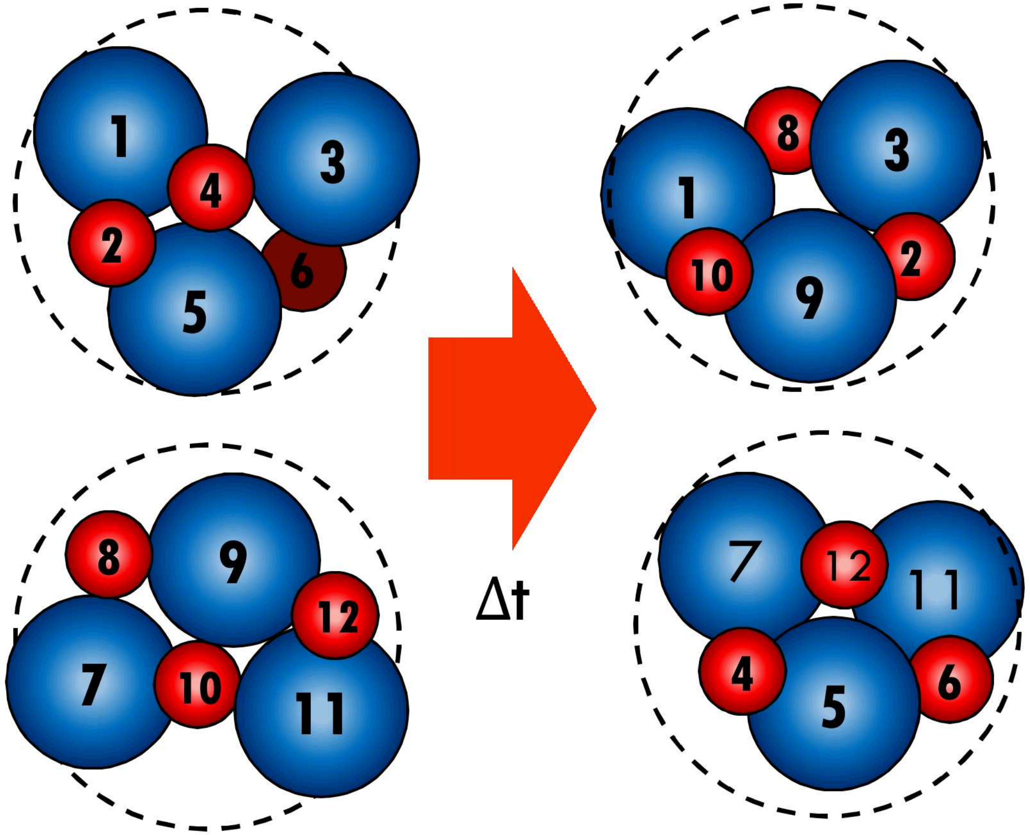

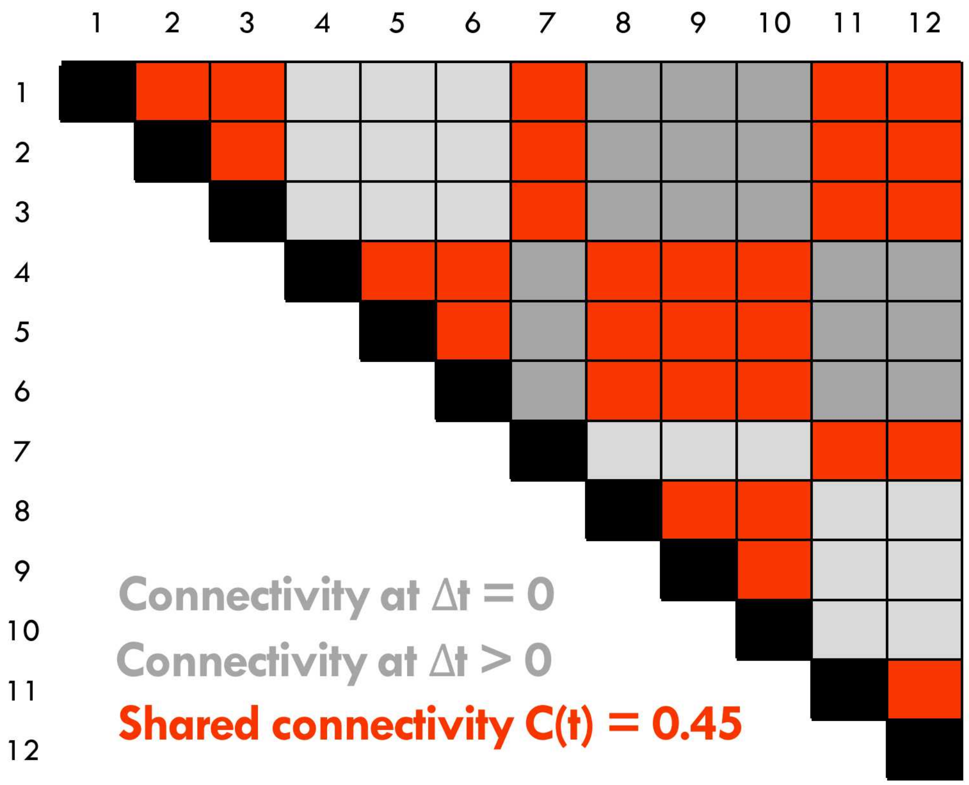

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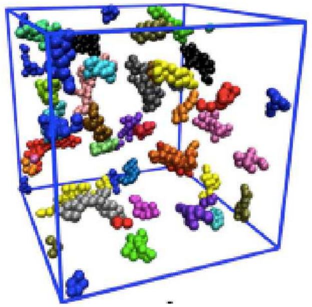
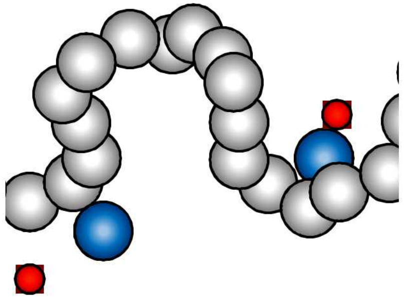
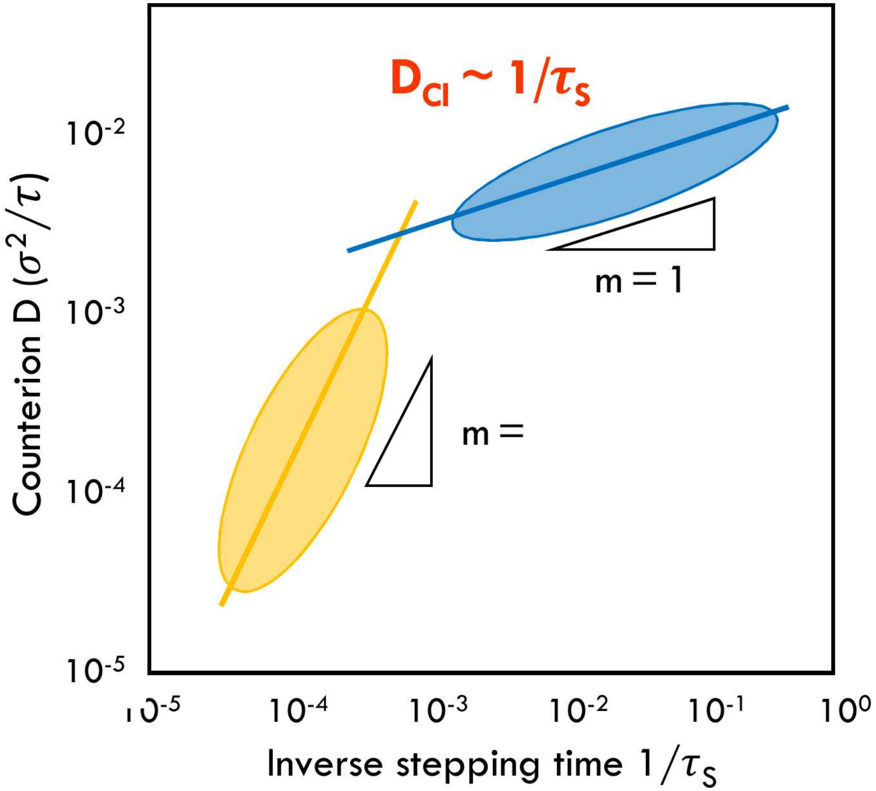
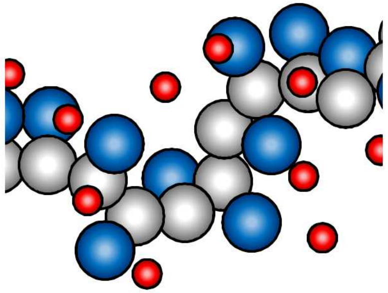


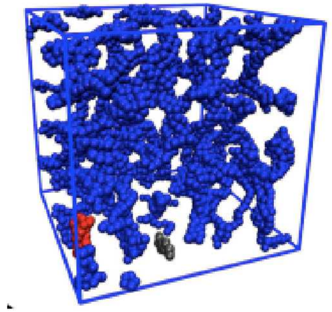
p13 polymer (sparse)







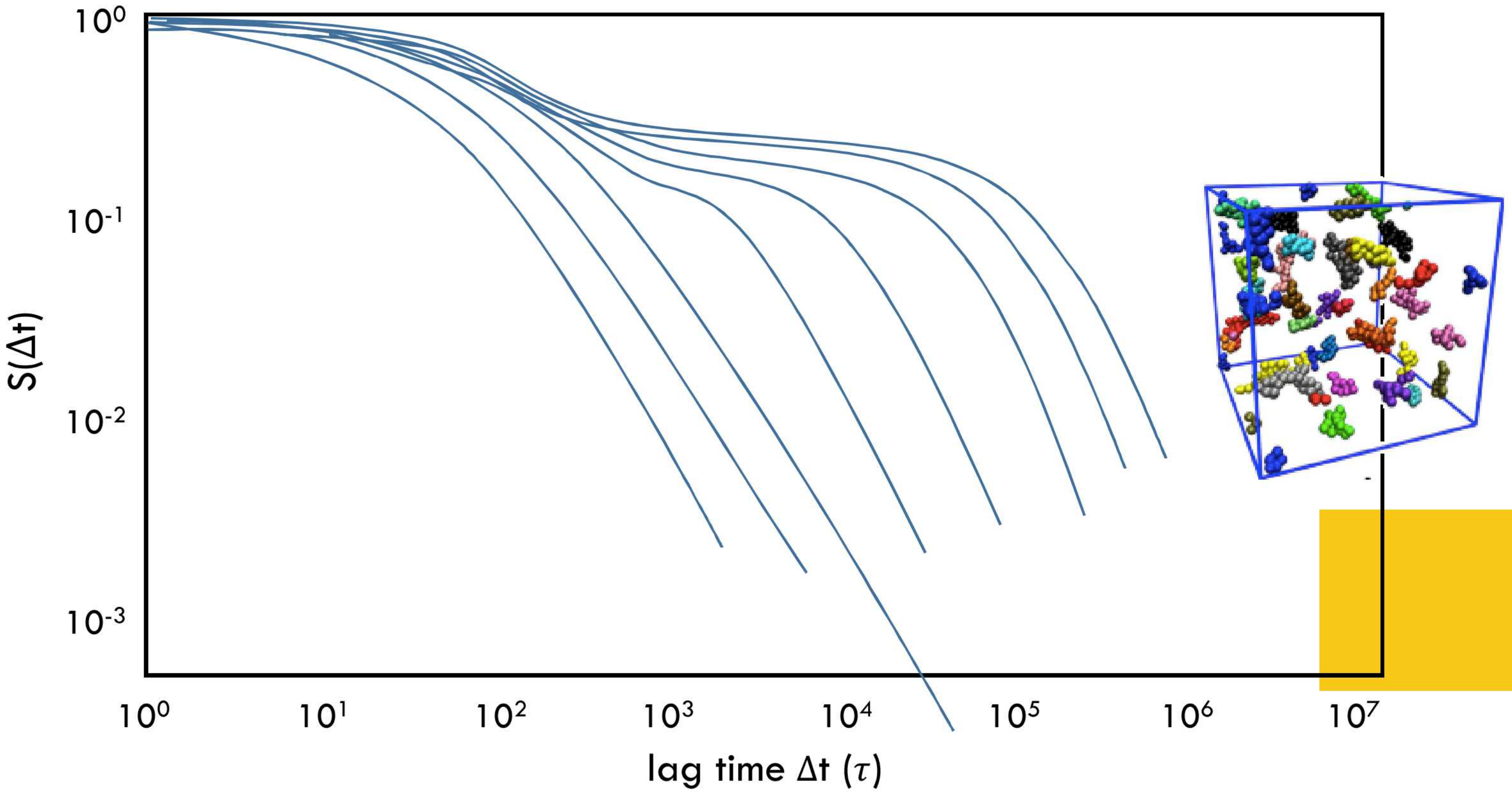
p1 polymer ("polyIL")



Characteristic stepping timescale predicts ion transport in networks—

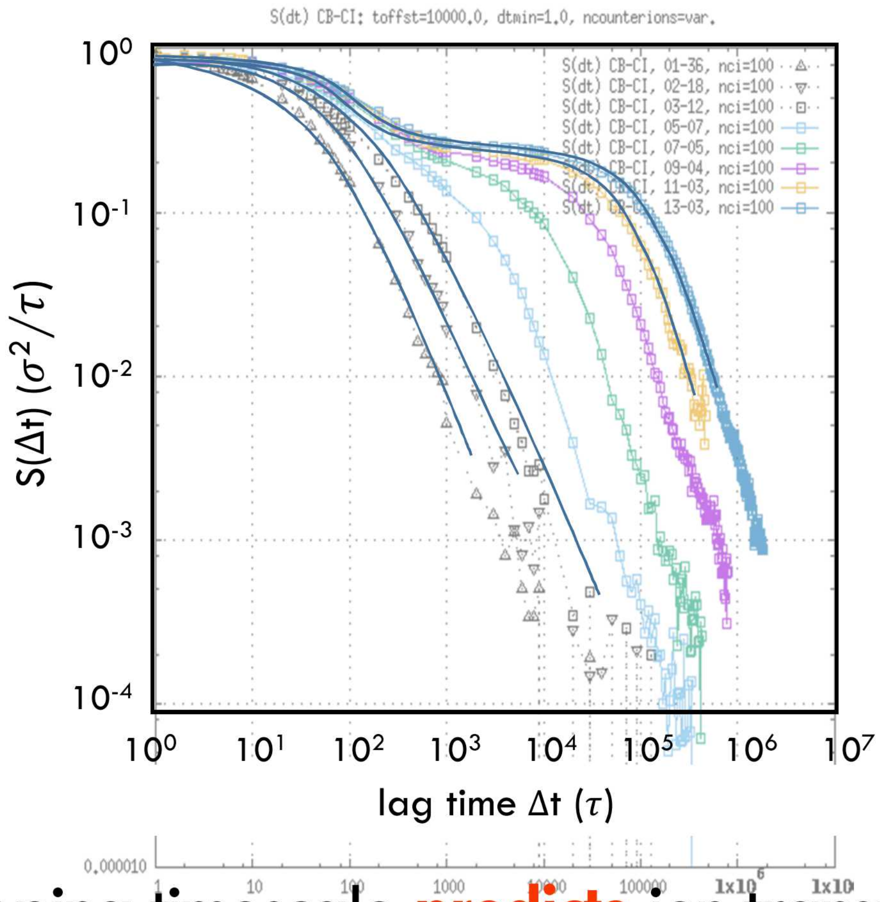
scales **incorrectly** for clusters (insufficient measure of connectivity?)

3) Physical mechanism(s) by which counterion diffusion occurs?



Characteristic stepping timescale **predicts** ion transport in networks—

3) Physical mechanism(s) by which counterion diffusion occurs?



Characteristic stepping timescale **predicts** ion transport in networks—