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Project 4: Gel Structure, Molecular Aggregation/Agglomeration and Gelation in Colloidal Fluids.

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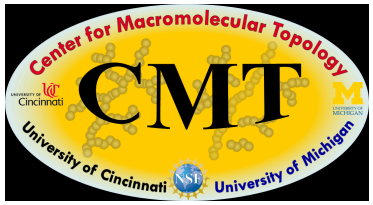
Proposed Budget: $150,000/year; In Kind Support Oak Ridge National Lab $40,000/year, National Institute of Standards an Technology $40,000/year

Project Duration: 3 years



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Outcomes/Deliverables

- Understanding the structure of gels and polymer aggregates/agglomerates using neutron scattering (SANS), x-ray scattering (SAXS), dynamic light scattering (DLS) and static light scattering (SALS).
- Understand thermodynamic basis for polymer aggregation, “phase-diagram”.
- Quantify gel structure, molecular weight between crosslinks, crosslink functionality from SANS measurement.

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Impact

- Understand gel product lines for synthetic control of properties.
- Ability to design and control gel functional properties.
- Understand complex rheological phenomena associated with polymer aggregation/ agglomeration.
- Relate complex colloidal rheology to chemistry and thermodynamic conditions.

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Prior work and project scope

- Identify relationship between rheological enhancement, polymer microstructure, and polymer chain chemistry in water soluble polymers and gels.
- Develop scattering and rheological methods to characterize aggregation and gelation in a range of systems including water soluble and water borne polymers
- Model samples for gel structure/property studies
- SANS on gels swollen in deuterated solvents
- Modeling of SANS with Gel-Tensile Blob Model for molecular weight between crosslinks, functionality and thermodynamics of gels
- Couple rheology and GTB model SANS results

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Prior work and project scope

The molecular architecture of polymer aggregates/agglomerates and swollen networks (gels) are not understood.

For gels, both the Flory-Rehner approach as well as the de Gennes c* model fail to describe structures commonly observed with neutron scattering.

For aggregation of aqueous polymers the structure model or a "phase diagram" model may be more appropriate to correlate aggregate/gel microstructure with measured rheological properties

Design of consumer products based on macromolecular topology of these materials is difficult in the absence of a viable structural model that agrees with structural measurements using SANS.

We have proposed the Gel-Tensile Blob Model that can be used to describe SANS measurements as well as to predict molecular weight between crosslinks, branch structure, branch functionality and thermodynamic characteristics of gels. A synthesis/structure/property relationship can be developed for these materials using this approach.

The project can couple efforts using SANS, theory, dynamic light scattering and rheology to develop a comprehensive understanding of gels, polymer aggregation and agglomeration in rheologically complex fluids.

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Supplementary Material

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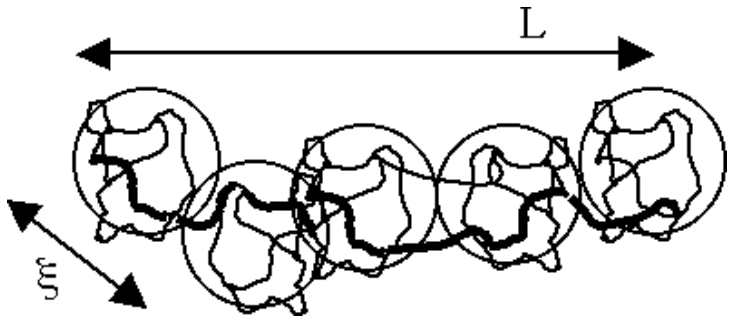

"Gel Tensile Blob" (GTB) Model

1) Disinterspersion
   Excluded Volume Expansion
2) Regions of High Topological Constraint Move Apart
   Due to Bulk Volume Expansion and Limited by
   Network Connectivity/Entanglements
3) Large Scale Structures are a Result, $L \sim N_{avg}Q^{1/2}$
4) Tensile Blobs Describe the Local Structure $\xi \sim kT/f$

Consider the equilibrium structure (Sequence is not known)

Sukumaran SK, Beaucage G *A structural model for equilibrium swollen networks* Europhys. Lett. **59** 714-720 (2002).

Panyukov S, Rubenstein M, *Explanation of anomalous scaling of swollen entangled chains* Macromolecules **38** 3511-3514 (2005).

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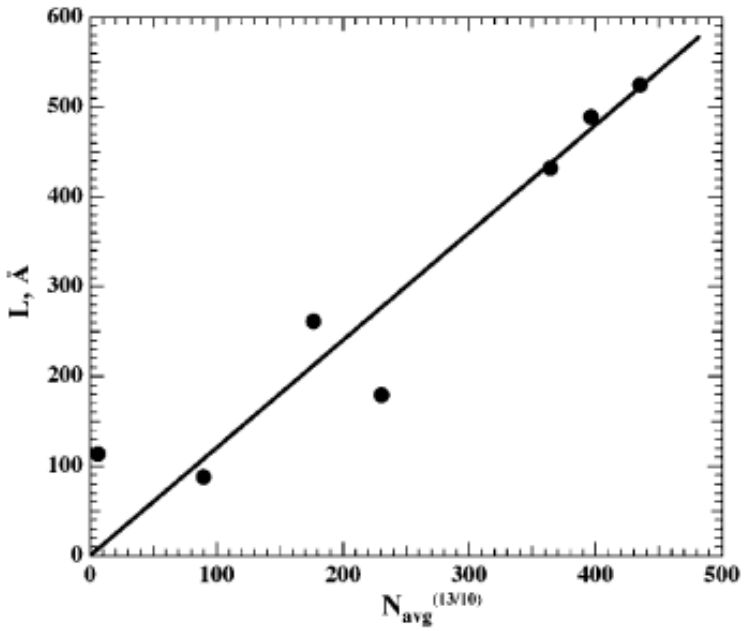
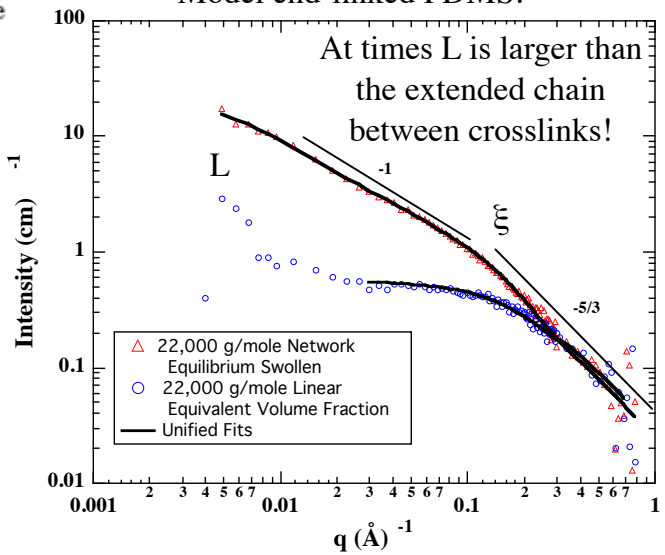


Fig. 9. *L versus* $N_{avg}^{(13/10)}$. The straight line passes through the origin as predicted by equation (12).

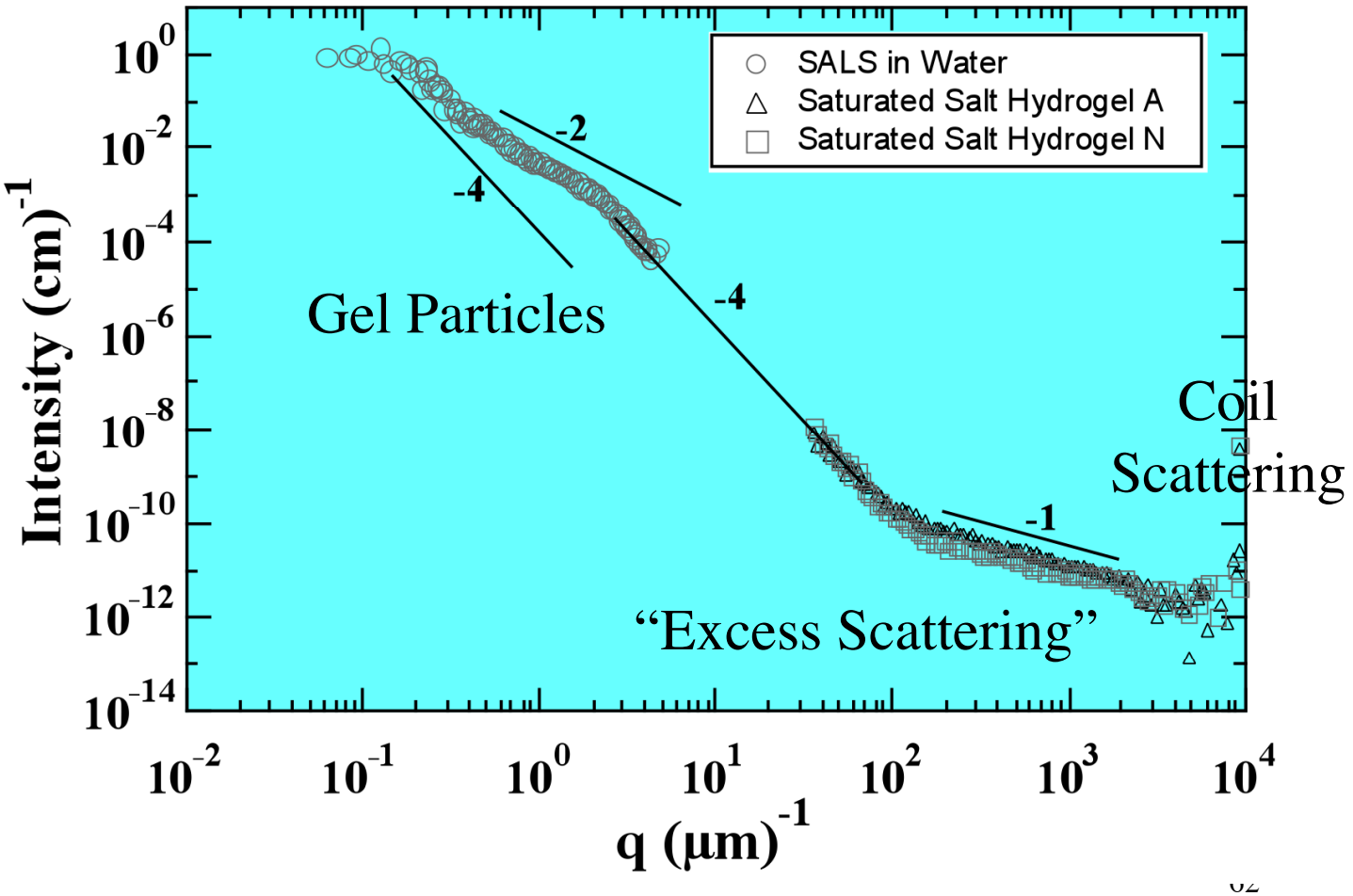
What is the source of excess, low angle scattering from equilibrium swollen gels?
Model end-linked PDMS.



Sukumaran SK, Beaucage G *A structural model for equilibrium swollen networks* Europhys. Lett. **59** 714-720 (2002).

Sukumaran SK, Beaucage G, Mark JE, Viers B, *Neutron scattering from equilibrium swollen networks* Eur. Phys. J. E **18** 29-36 (2005).

Light and Neutron Scattering from a Equilibrium Swollen Superabsorbant Hydrogel



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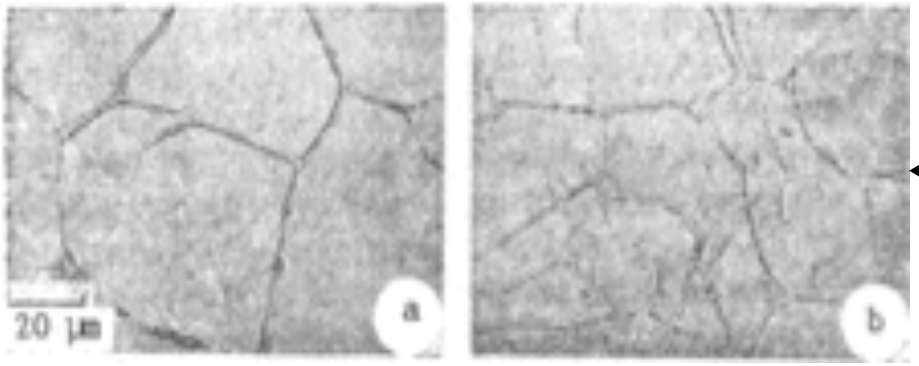
Why study microstructure?

For example: structure matters for Poly(ethylene) oxide (PEO) drag reduction.

Aggregate Structure ↔ **Fast pipeline transport**



(Kalashnikov et al., Inzhenerno-Fizicheskii Zhurnal 1990)

PEO will yield greater improvement per unit mass because of its aggregate structure.

* Photo compiled from online source

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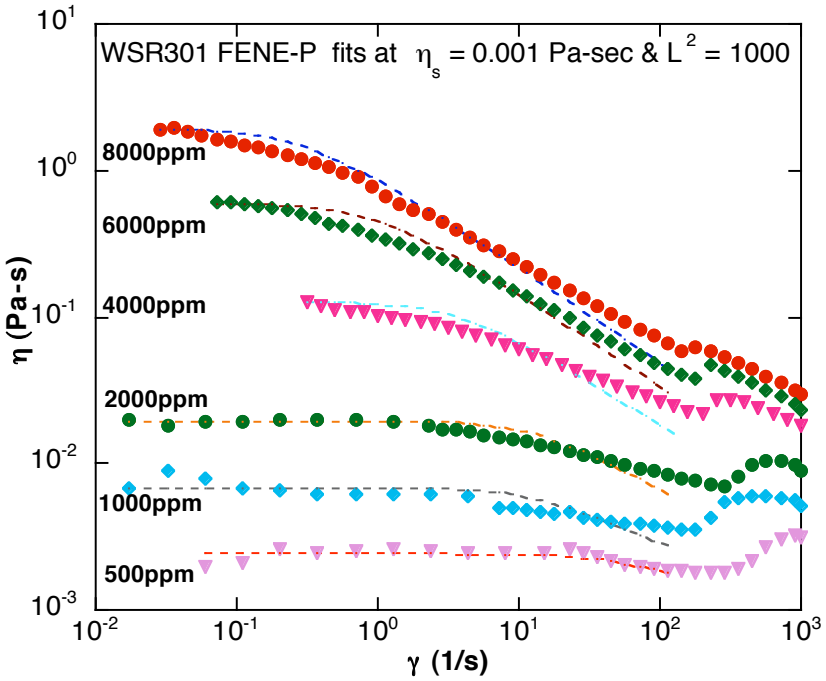
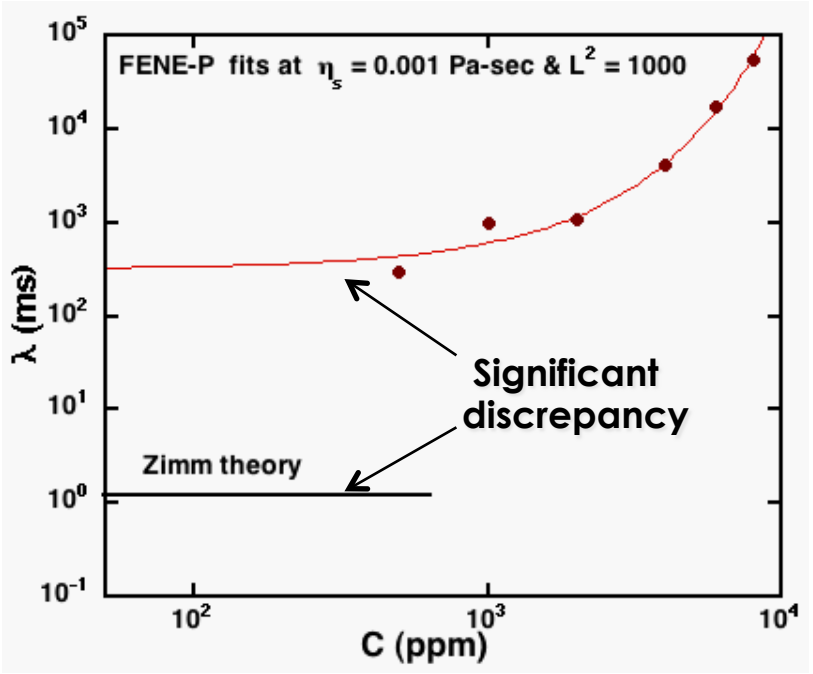
Anomalous PEO Rheology





Molecular structure of PEO not consistent with that of isolated polymer chains.

Work done in collaboration with Ron Larson, Youngsuk Heo, Bamin Khomani, Eric Shaqfeh and Radhakrishnan Sureshkumar.

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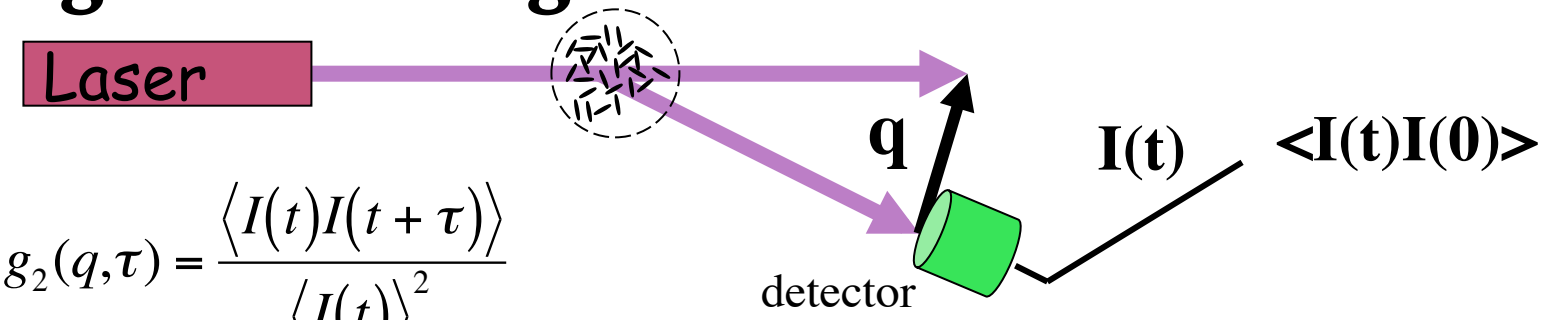
Collective dynamics by means of dynamic light scattering

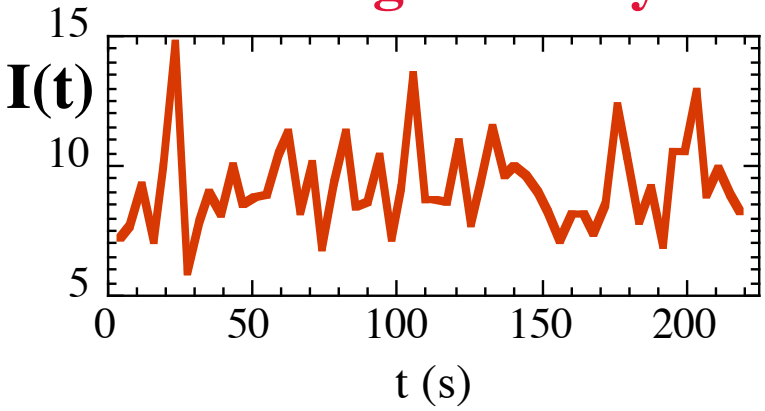


$$g_2(q,\tau) = \frac{\langle I(t)I(t+\tau)\rangle}{\langle I(t)\rangle^2}$$

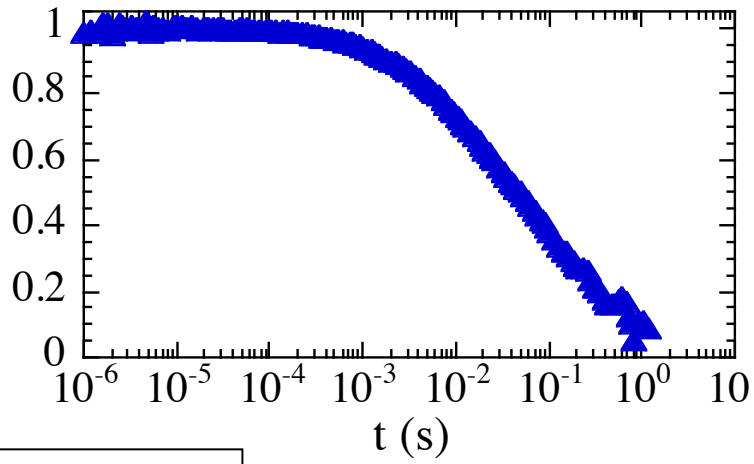
$$g_2(q,\tau) = 1 + \beta\left|f(q,t)\right|^2$$

$$f(q,t) = \frac{1}{N}\left\langle \sum_{i,j} \exp(i\mathbf{q}\bullet\left[\mathbf{r}_i(0) - \mathbf{r}_j(t)\right]\right\rangle$$

Scattering Intensity → **Dynamic Structure Factor**



f(q,t)



Special methods for non-ergodic samples: Pusey and van Megen, 1989

$$5 \le q \le 25\mu m^{-1}$$

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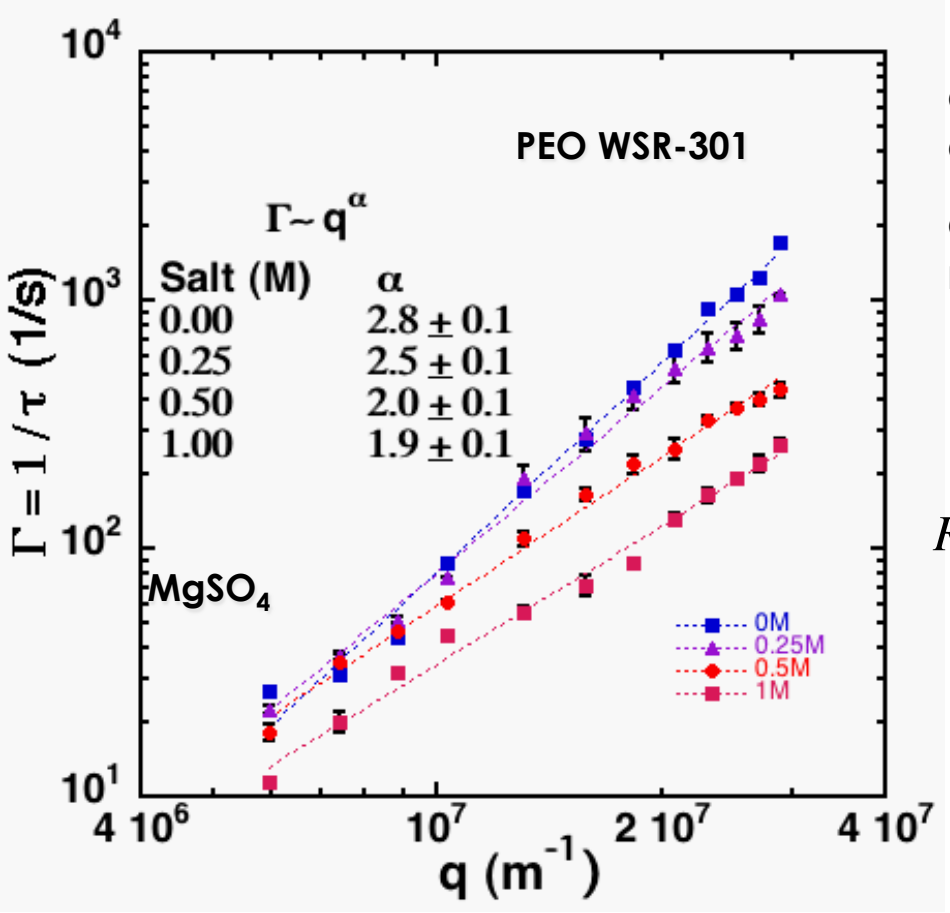
Modifying aggregate structure: Magnesium sulfate



$qR_h << 1$: Center of mass diffusion : $\Gamma \sim q^2$

$qR_h >> 1$: Internal coil motions : $\Gamma \sim q^3$

$$R_h = \frac{k_B T}{6\pi\eta D} \sim 290nm \rightarrow M_w \sim 3\times10^7$$

$\Gamma \sim q^3$ (No salt) ⟶ $\Gamma \sim Dq^2$ (With salt)

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