Student Introductions

1) Roddel Remy
2) Paul Godfrin
3) Avantika Singh
4) Taini Yang
5) Erika Saffer
6) Erbu Kizilay
7) Bradley Frieberg
8) Nolan Gallagher
9) Wei-Shao Tung
10) Michael Hore
11) Chaitra Deodhar
12) Gregory Newbloom
13) Adriana Campos-Ramirez
14) Gualberto Ojeda Mendoza
15) Ashley Hart
16) Mekonnen Lemma Dechassa
17) Tao Yu
18) Derrick Swinton
19) Zhe Wang
20) Amit Patel
21) Yining Xia
22) Shih-Chun Huang
23) Enpeng Du
24) Maria Monica Castellanos
25) Michael Hoepfner
26) Hari Katepalli
27) Mangesh Chaudhari
28) Xiaoming Zhu
29) Ankitkumar Fajalia
30) Jinkun Hao
31) Sebastian Jezowski
32) Charles Heffern
33) Kelly Forney
34) Yingchao Chen
35) Trong Pham
36) Garfield Warren

UNIVERSITY of DELAWARE

Department of Materials Science and Engineering

Group Advisor :- Prof. Michael Mackay

Group Members :- Brett Guralnick, Hao Shen, Jeong Jae Wie, Wenluan Zhang, Roddel Remy, Ngoc Nguyen, Robert Jones, Lan Li

Polymer/Nanoparticle Blends

- Nanoparticle dispersion in polymer matrices (TEM, SAXS, SANS, AFM)
- Rheological characterization of polymer melts
- Tensile properties at Glassy States

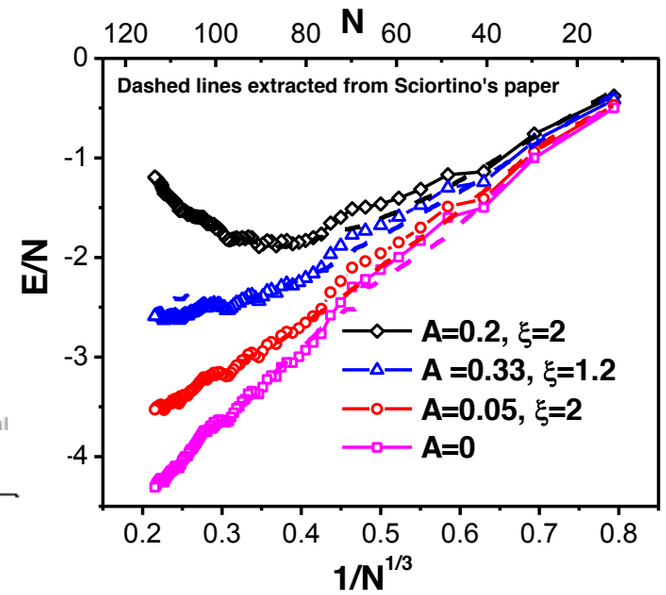
Polymer-based Solar Cells

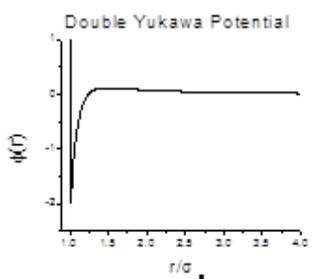
- Device characterization (J-V measurements)
- Active layer morphology characterization (SAXS, XRD, SANS, NR)
- Interfacial phenomena between active layer and contacts (AFM)
- Effect of processing conditions on device performance

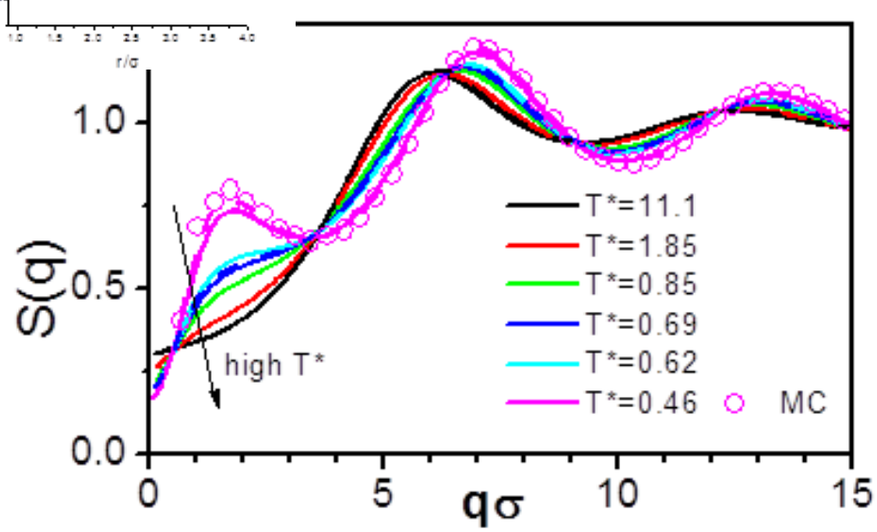
P. Douglas Godfrin – Wagner Group (UD)

Structure-Property Relationship of Cluster Forming Colloids

Certain colloids have been found to form stable aggregates of specific size under competing attraction and repulsion

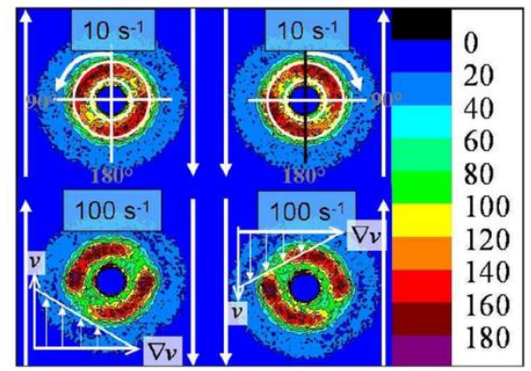


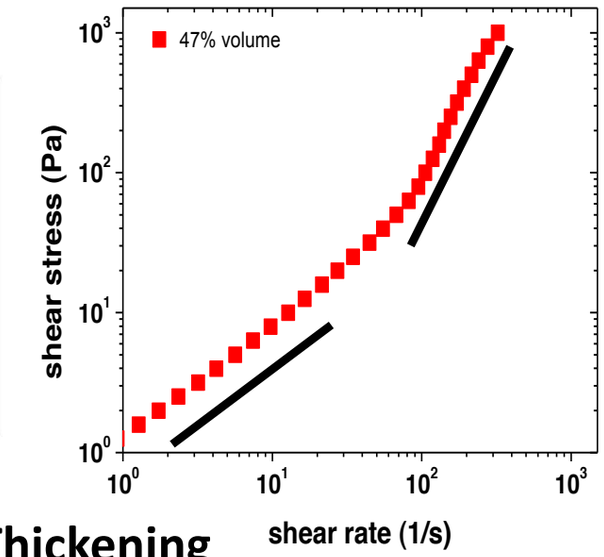




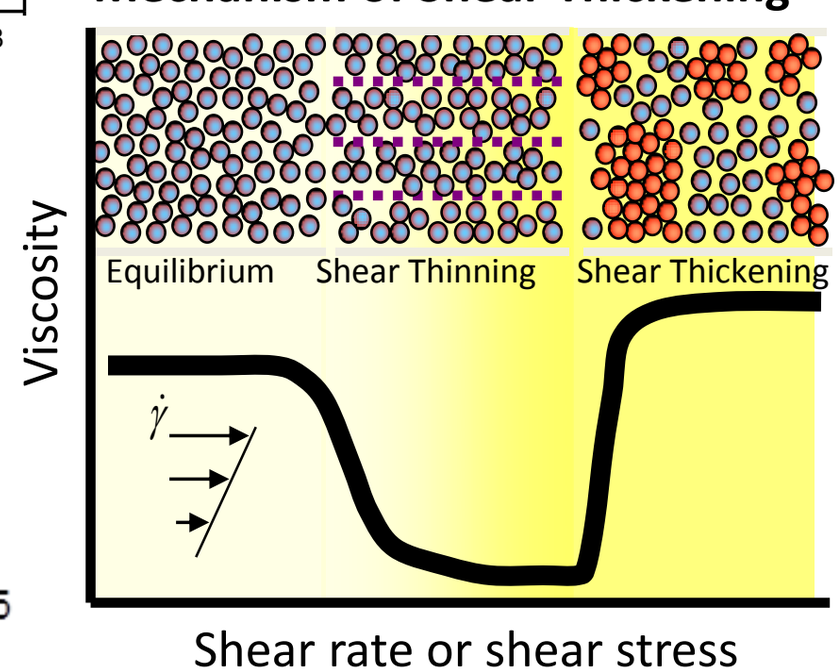
SANS is used to probe the presence of an "intermediate range order peak" in the structure factor characteristic of cluster formation

Rheology of Shear Thickening Fluids





Mechanism of Shear Thickening



Rheology shows a drastic increase in viscosity with increasing shear rate of shear thickening fluids.

Combined with SANS, shows formation of "hydroclusters"

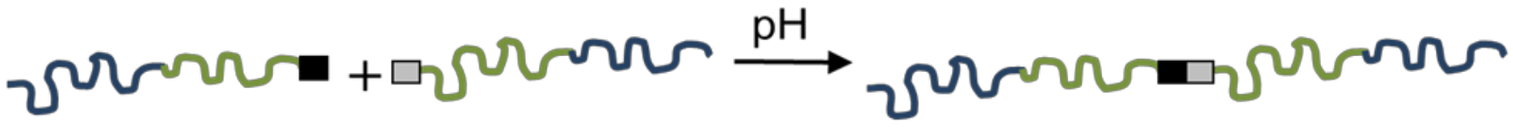
Possible applications of STFs: (1) body armor (2) sports equipment

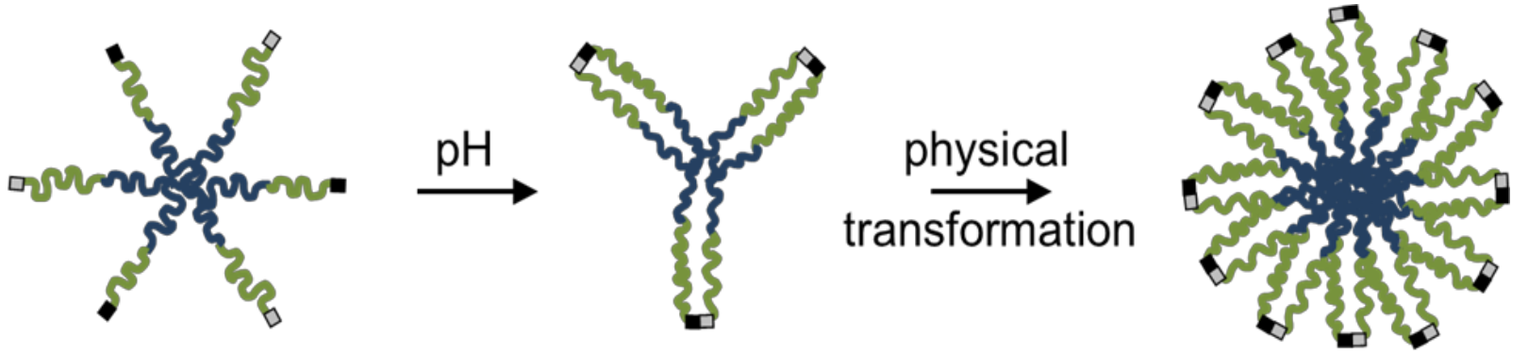
Biodegradable Polymers for Biomedical Applications

Avantika Singh, Dr. Megan Robertson

- Functionalization of amphiphilic polymers with reactive entities, and investigation of their controlled coupling and resulting morphological changes.

  Applications : Organic nanoreactors and controlled drug delivery devices.
- Characterization of the relevant thermodynamic and kinetic processes that govern the evolution of polymer characteristics.





Star-like spherical micelle chemical coupling Flowerlike micelle, evolves to its equilibrium size & aggregation number

Synthesis and end-group functionalization of diblock copolymers → Optimization of click chemistry-based coupling reaction → Light and neutron scattering experiments to probe the structural transformation → Determination of the self-assembly mechanism in the presence and absence of core crystallization through comparison of data and theory

UNIVERSITY of HOUSTON
CULLEN COLLEGE of ENGINEERING

THE PHASE BEHAVIOR OF THE TRAPPED HYDROGEN AT DISLOCATIONS

Material: Deformed Palladium (Pd)

Condition: 5, 300 K ; with and without H_2

Methods:

IINS (Incoherent Inelastic Neutron Scattering)

-information for VDOS

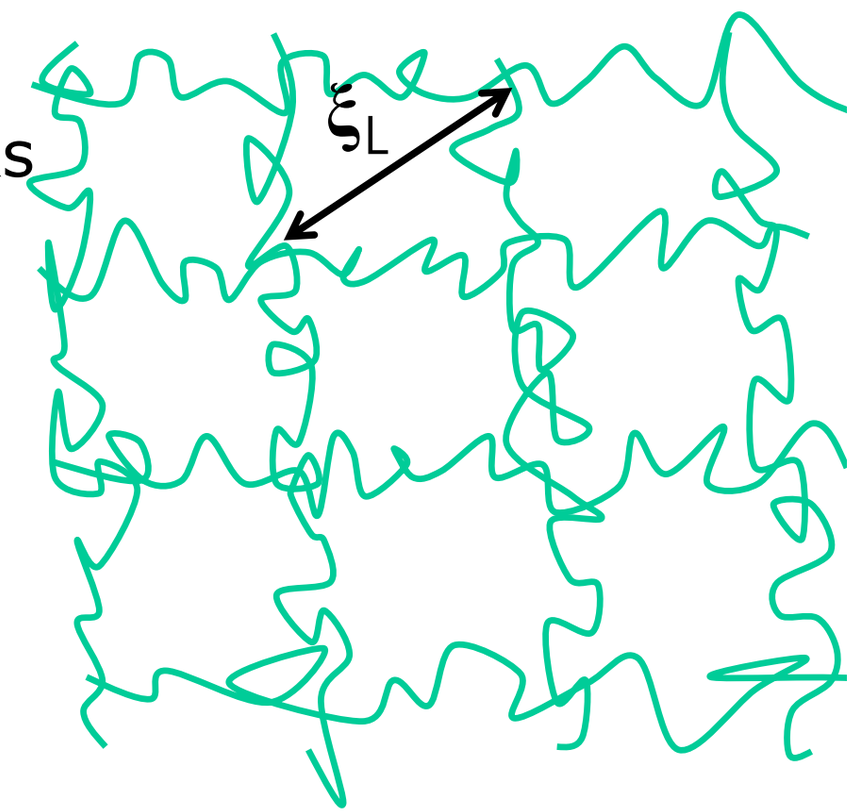
SANS (Small Angle Neutron Scattering)

-Spatial profile of deformed Pd

Poly(ethylene glycol) Hydrogels with Novel Network Structures

- Research in Biomaterials
  - Develop hydrogels for biomaterial applications

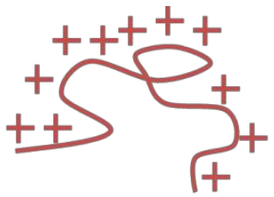
- PEG-based hydrogels with a tetra-functional cross-linker
  - Control distance between cross-links
  - Reduce inhomogeneities
  - Increase elastic modulus



- Characterization with SANS supports that this type of network is present

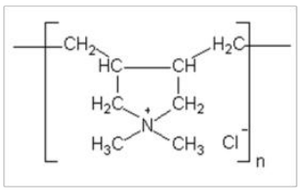
Phase Transitions in Polyelectrolyte-Mixed Micelle Systems

Complex coacervation: separation of a macromolecular solution - composed of two oppositely charged macroions - into two immiscible liquid phases



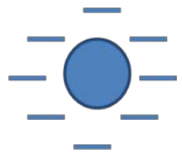
Polycation PDADMAC

Poly(diallyldimethylammoniumchloride)



R_g ~ 35 nm (Mn = 270K)

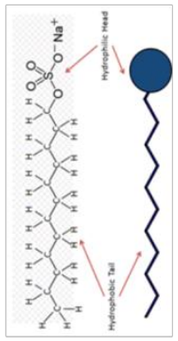
R_g ~ 15 nm (Mn = 90K)



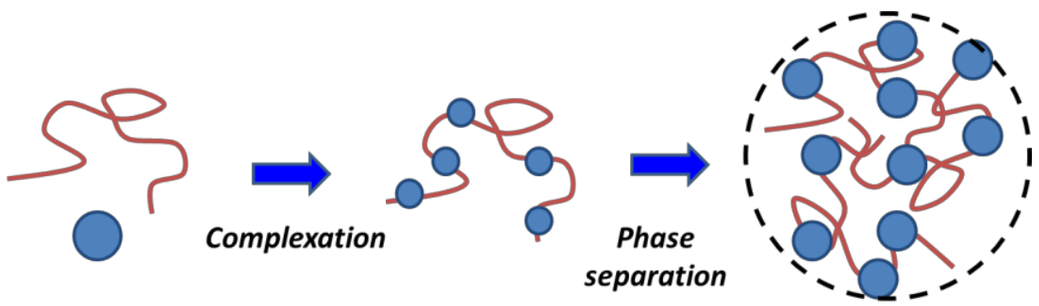
~ r = 8nm

Anionic-nonionic mixed micelle

Sodium dodecylsulphate SDS/Triton X100



in 0.4 M NaCl aqueous solution

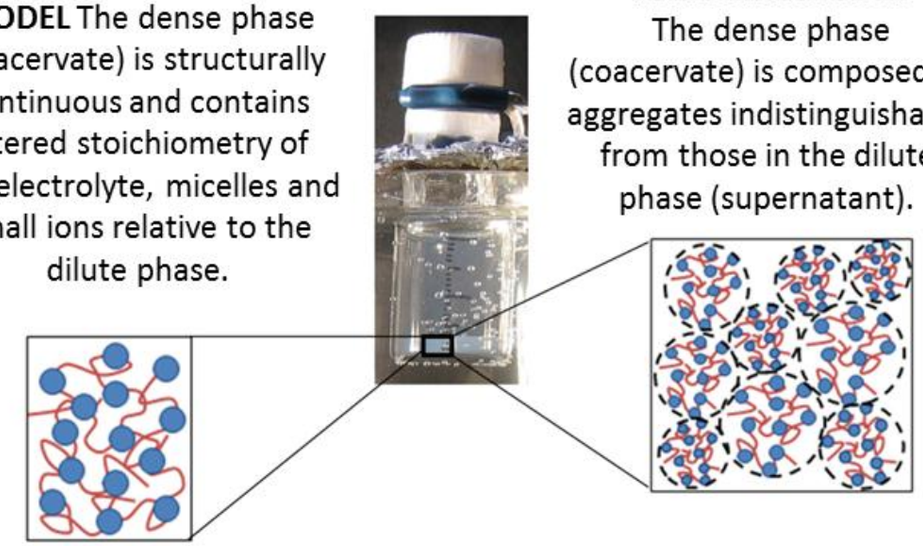


It can be Induced by changing [+]/[-] via: ionic strength, stoichiometry of the two macromolecules (polyelectrolyte/micelles ratio in our case), charge density of the two macromolecules (linear charge density for polyelectrolytes through molecular weight and surface charge ratio for micelles through anionic/nonionic surfactant ratio).

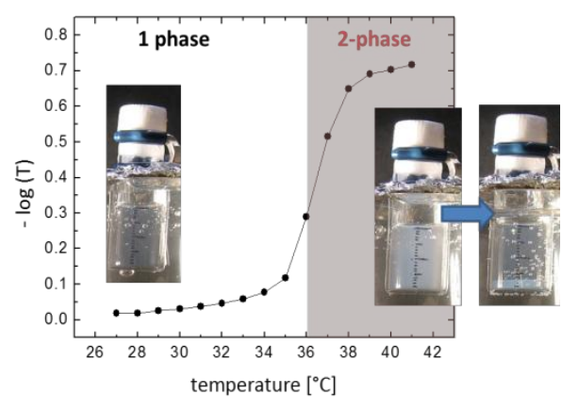
How do the aggregates interact and give rise to phase separation?

***CLASSICAL* COACERVATION MODEL** The dense phase (coacervate) is structurally continuous and contains altered stoichiometry of polyelectrolyte, micelles and small ions relative to the dilute phase.

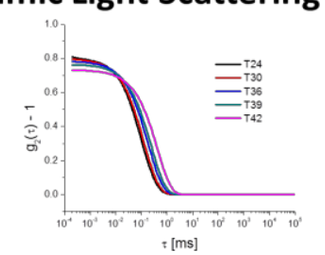
***COLLOIDAL* MODEL** The dense phase (coacervate) is composed of aggregates indistinguishable from those in the dilute phase (supernatant).



Turbidimetry

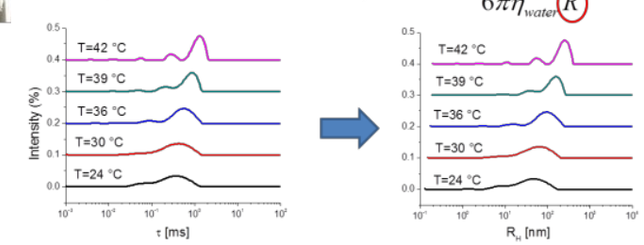


Dynamic Light Scattering (DLS)



Fit by CONTIN method: $g_1(\tau) = \sqrt{g_2(\tau) - 1} = \int dD P(D) \exp(-q^2 D \tau)$

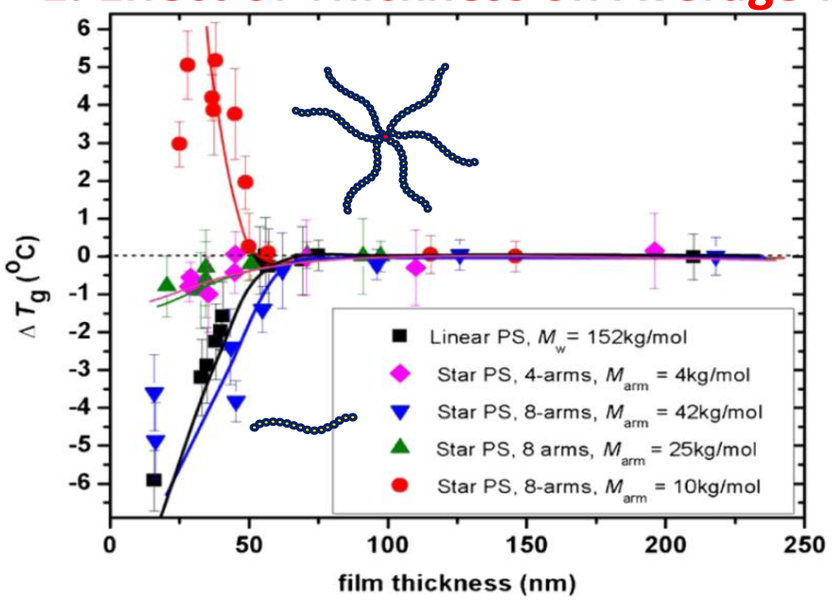
$$g_1(\tau) = \exp(-q^2 D \tau) \rightarrow D = \frac{k_B T}{6\pi\eta_{water} R}$$



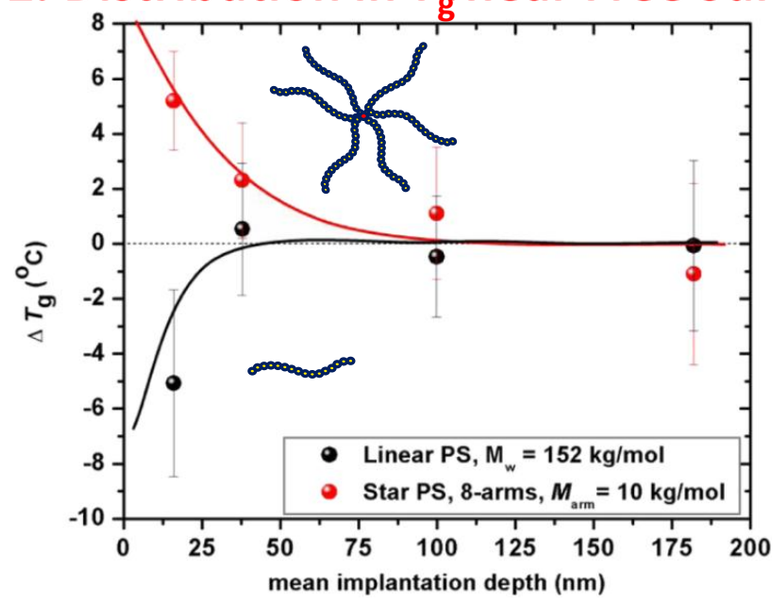
Effect of Polymer Architecture on the Physical Properties of Thin Supported Films

Bradley Frieberg, University of Michigan, Dr. Peter Green's Group

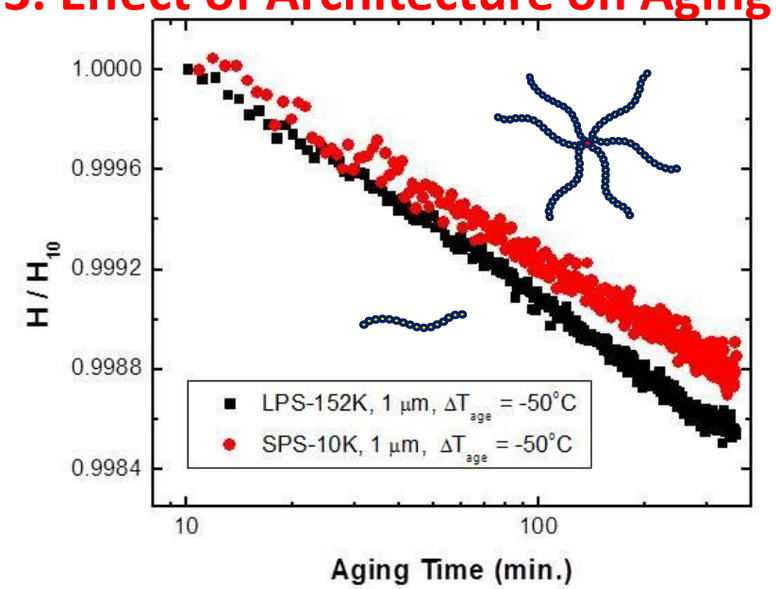
1. Effect of Thickness on Average T_g[1]



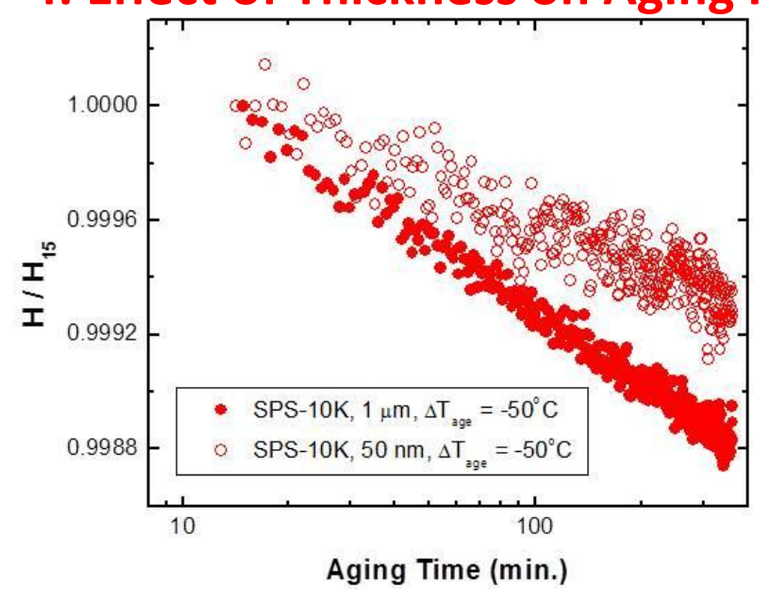
2. Distribution in T_g near Free Surface[1]



3. Effect of Architecture on Aging Rate[2]



4. Effect of Thickness on Aging Rate[3]



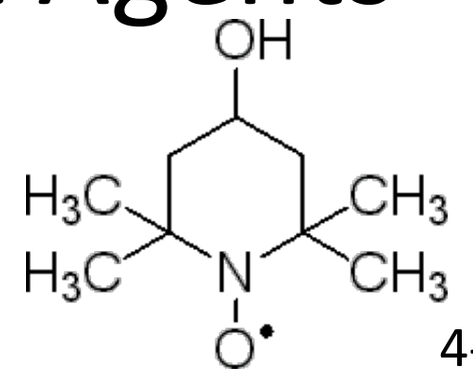
THE GREEN GROUP
LABORATORY FOR COMPLEX MATERIALS RESEARCH

[1]Glynos, E., Frieberg, B. , Oh, H., Liu, M., Gidley, D.W., Green, P.F., *Phys. Rev. Lett.* **106** (2011)
[2]Frieberg, B., Glynos, E., Green, P.F., *Submitted for publication*
[3]Frieberg, B., Glynos, E., Green, P.F., *Submitted for publication*

Nolan Gallagher- University of Nebraska at Lincoln – Rajca Research Group

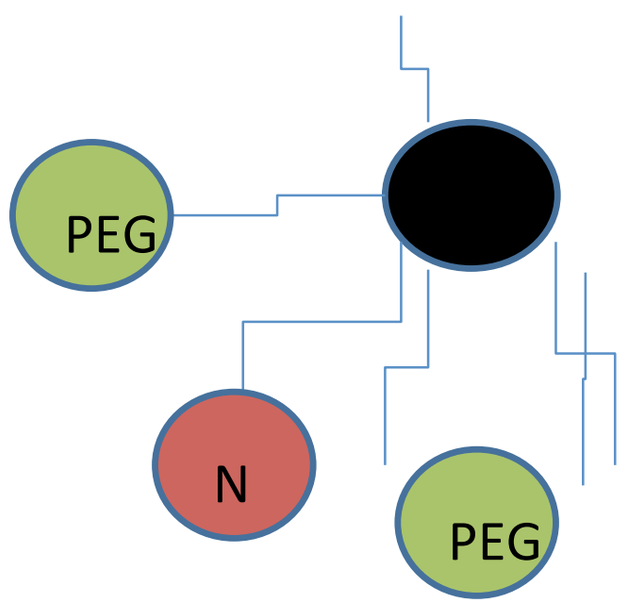
Nitroxide Radicals as a Replacement for MRI Contrast Agents

- Current MRI contrast agent (Gadolinium-based materials) has shown toxicity and has been issued a "black box warning" by FDA in 2007
- A replacement MRI contrast agent should be non-toxic, non-immunogenic, stable, water soluble, and effective (high relaxivity)
- One option currently being explored in our group is nitroxide-based materials



4-HydroxyTEMPO, a simple nitroxide

A Nitroxide/ PEG based dendrimer

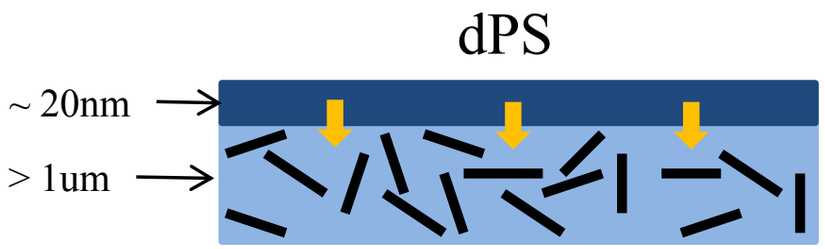


- Our group has designed several dendrimers with PEG (polyethylene glycol) and different nitroxides attached to the surface; these show promising properties when tested on mice
- SANS would enable us to see the exact shape of these dendrimers and how water interacts with the surface
- This could lead to the design of dendrimers with higher relaxivity and more effective imaging

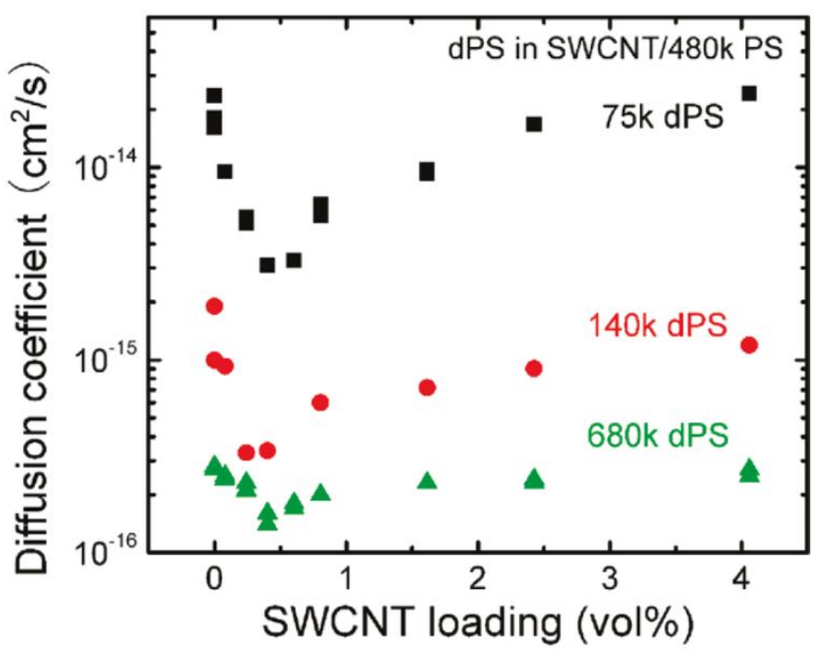
Polymer Diffusion in Nanocomposites

Wei-Shao Tung, University of Pennsylvania

Cylindrical Nanoparticles

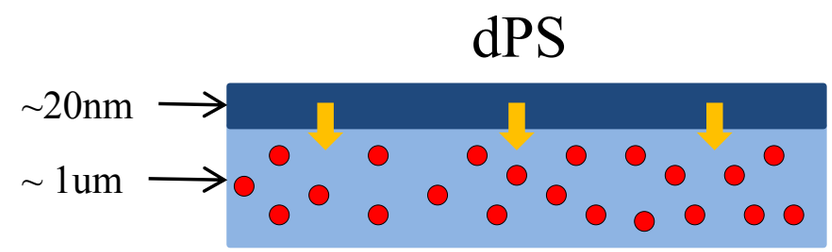


PS/Single-Walled Carbon Nanotubes

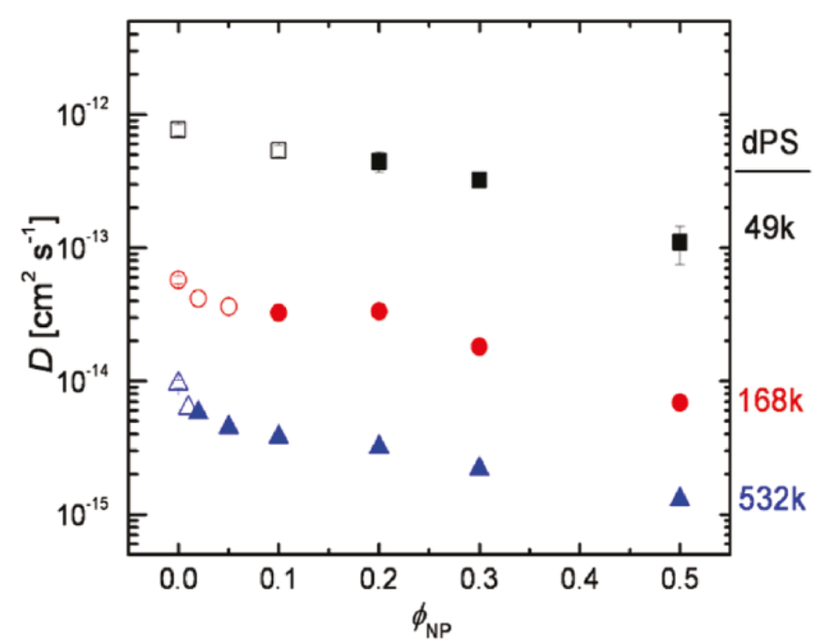


Mu, Clarke, Composto, Winey
Macromolecules 2009, 42, 7091-7097

Spherical Nanoparticles



PS/Phenyl-capped Silica Nanoparticles



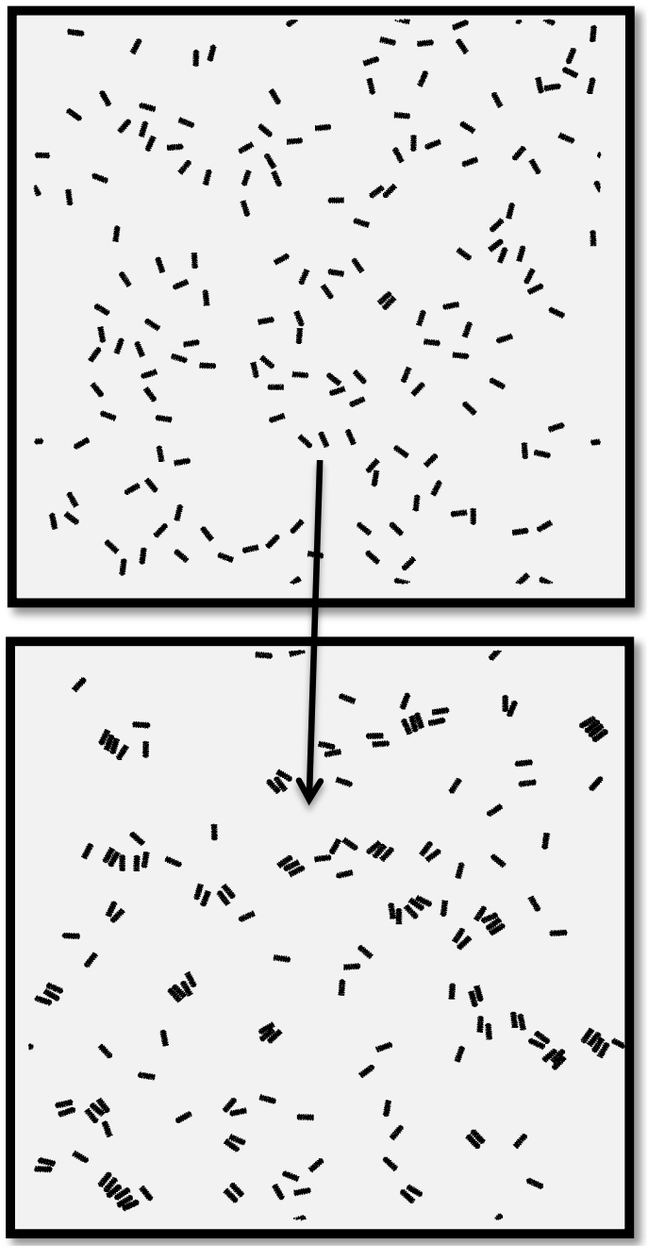
Gam, Meth, Zane, Chi, Wood, Seitz, Winey, Clark, Composto
Macromolecules 2011, 44, 3494-3501

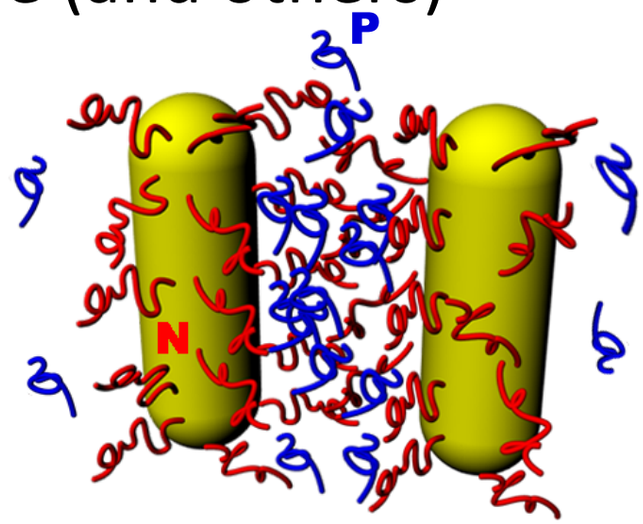
Composto Polymer Research Group

Advisor: Russell J. Composto

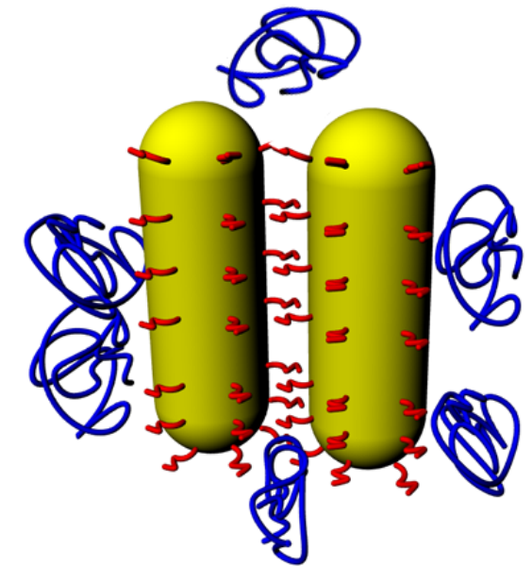
Members: Michael Hore (and others)

Monte Carlo Simulations



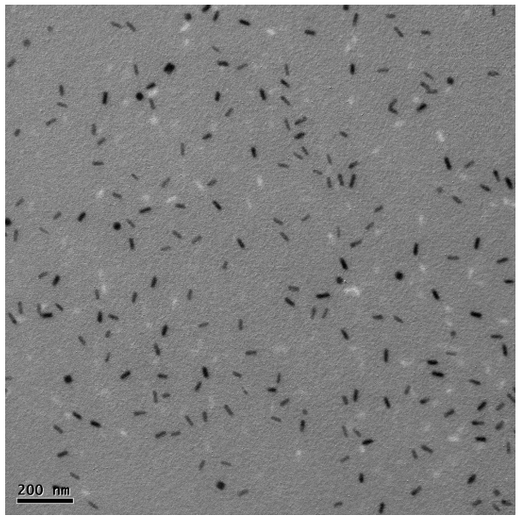


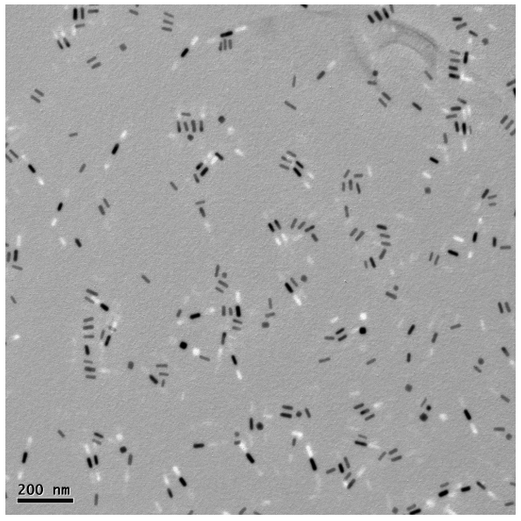
P < 3N
Dispersion
No change in surface plasmon resonance



P > 3N
Aggregation
Blue shift of surface plasmon resonance

Experiments





Structure and Swelling Behavior of Weak Polyelectrolyte Brushes

Chaitra Deodhar[1] S.Michael Kilbey II[1,2]

[1] Department of Chemistry, University of Tennessee, Knoxville, TN 37996

[2] Center for Nanophase Materials Sciences, Oak Ridge National Laboratory, Oak Ridge, TN, 37831

THE UNIVERSITY of TENNESSEE KNOXVILLE

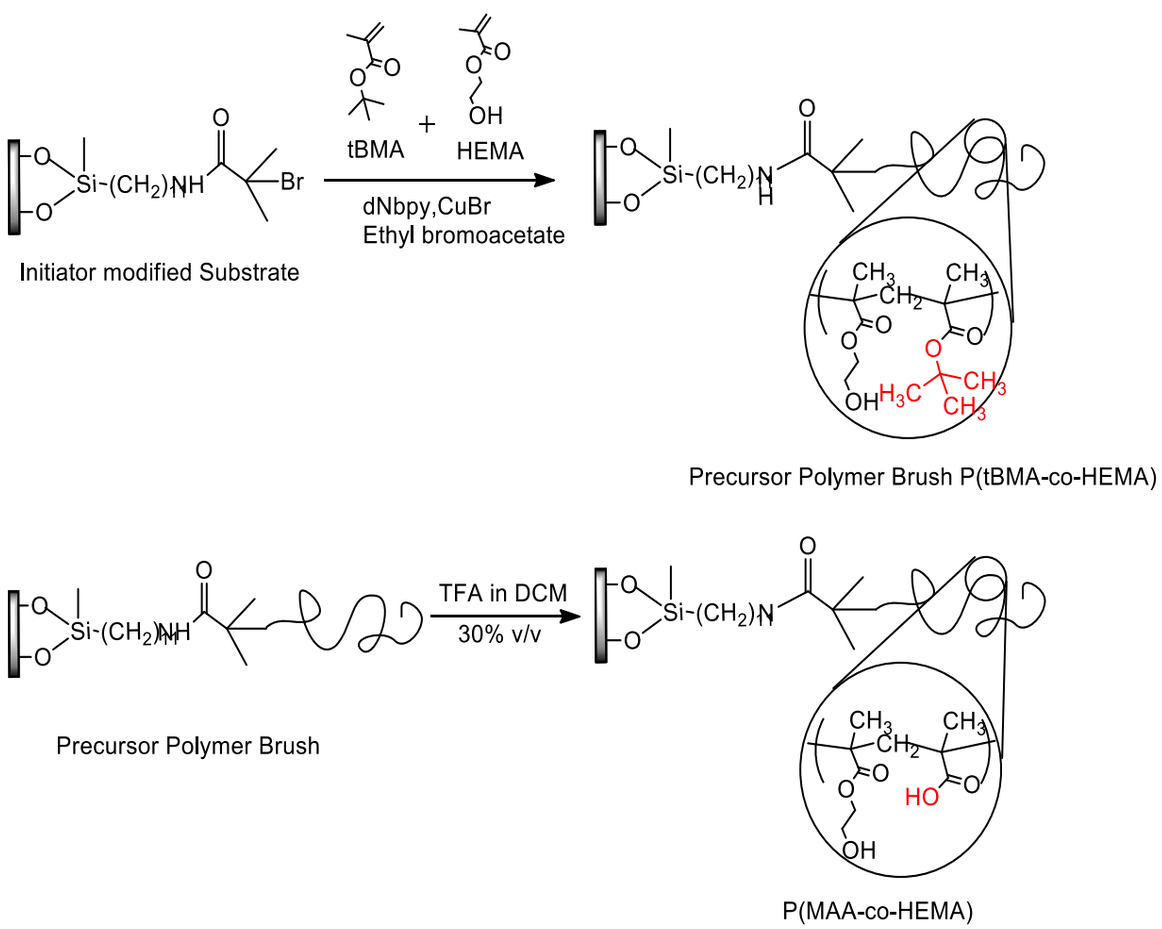
Introduction

Through this work I seek to understand the connections between the charge and conformations in polyelectrolyte (PE) brushes

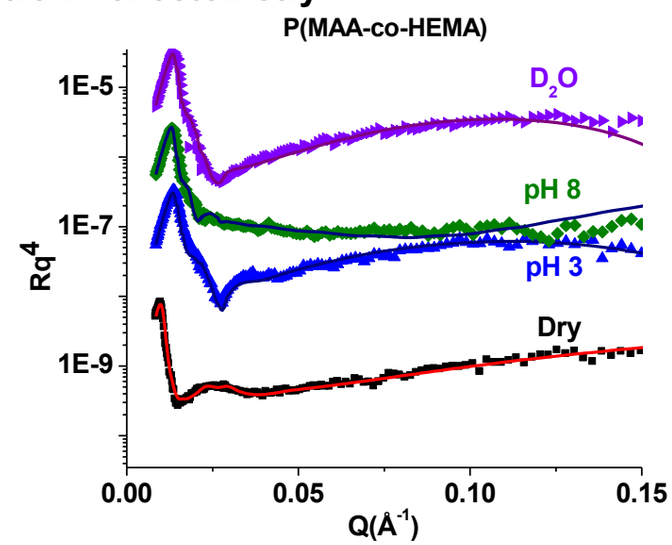
- Complexity in the structure of PEs arise due to the fact they contain ionizable repeat units.
- As the properties of PE brushes depend on the molecular conformation, it is important to understand how their structure is affected by charge.
- Neutron reflectometry (NR) and ellipsometry are used to characterize the nanoscale structure of the PMAA and P(MAA-co-HEMA) brushes.

Experimental

Scheme for the Synthesis of P(MAA-co-HEMA) brushes



Neutron Reflectometry



Brush	Nb ($Å^{-2}$)	d (Å)	σ (Å)
Dry	7.4×10^{-6}	219.0	139.5
pH 3	3.69×10^{-6}	352.8	162.0
D_2O	3.52×10^{-6}	368.8	235.0
pH 8	4.69×10^{-6}	671.8	180.0

Conclusions

- Successfully determined segment density profiles from well-defined, negatively charged MAA containing brushes.

I will continue to pursue careful studies of pH responsive brushes to determine how conditions set by synthesis affects the structure and responsiveness.

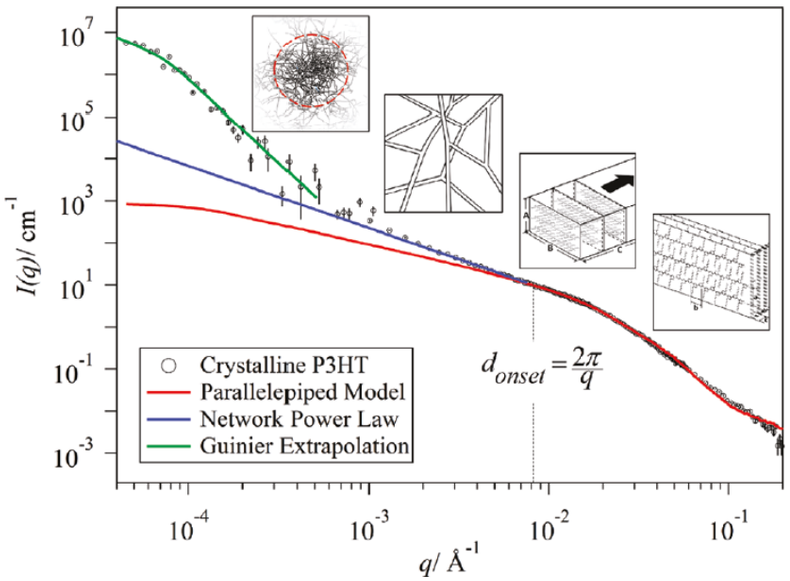
Gregory Newbloom

University of Washington, Department of Chemical Engineering
Advisor: Professor Danilo C. Pozzo

Renewable Energy Technology

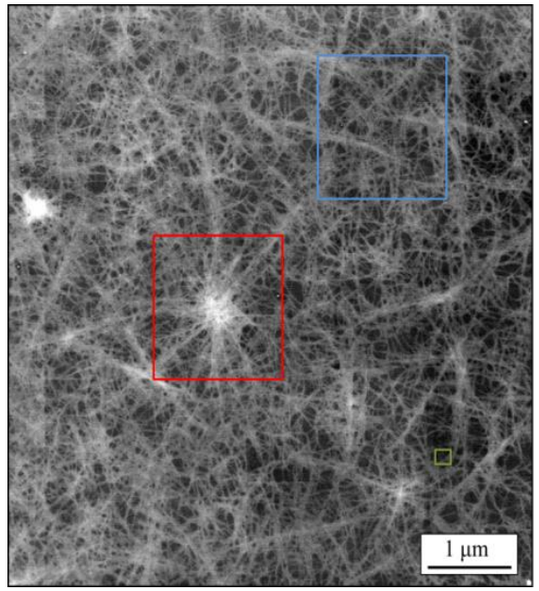
Konarka Power Plastics©

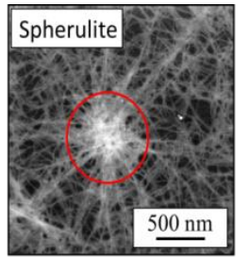
Multi-scale Analysis is Critical

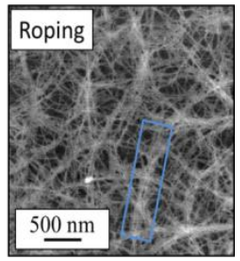


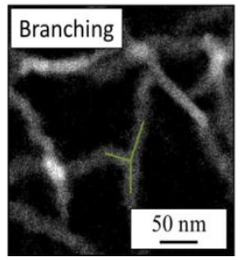
Newbloom et al., Mesoscale Morphology and Charge Transport in Colloidal Networks of Poly(3-hexylthiophene), *Macromolecules*, 2011, *44* (10), pp 3801-3809

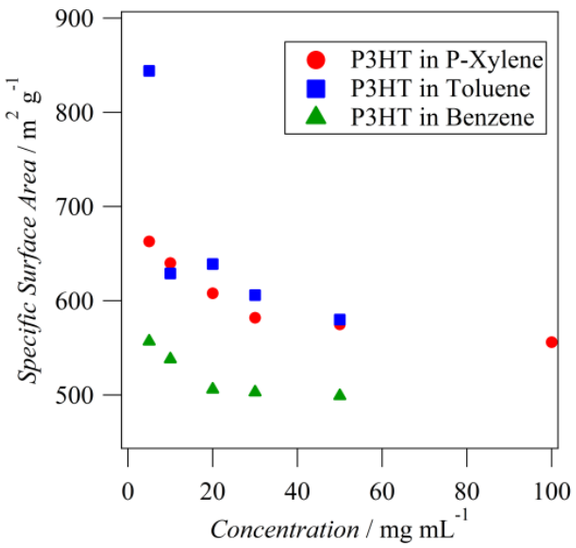
Designing the Ideal Photoactive Layer

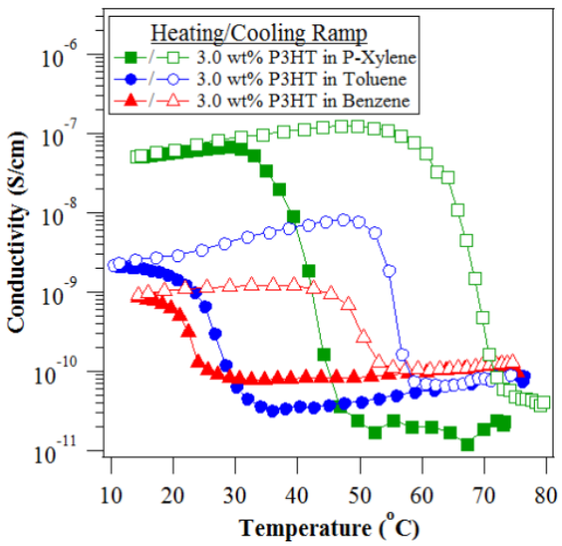












Soft Condensed Matter

Physics Departament

Cinvestav

Theory, Numerical Simulations and Experiments of Colloidal Suspensions

Polymeric Solutions

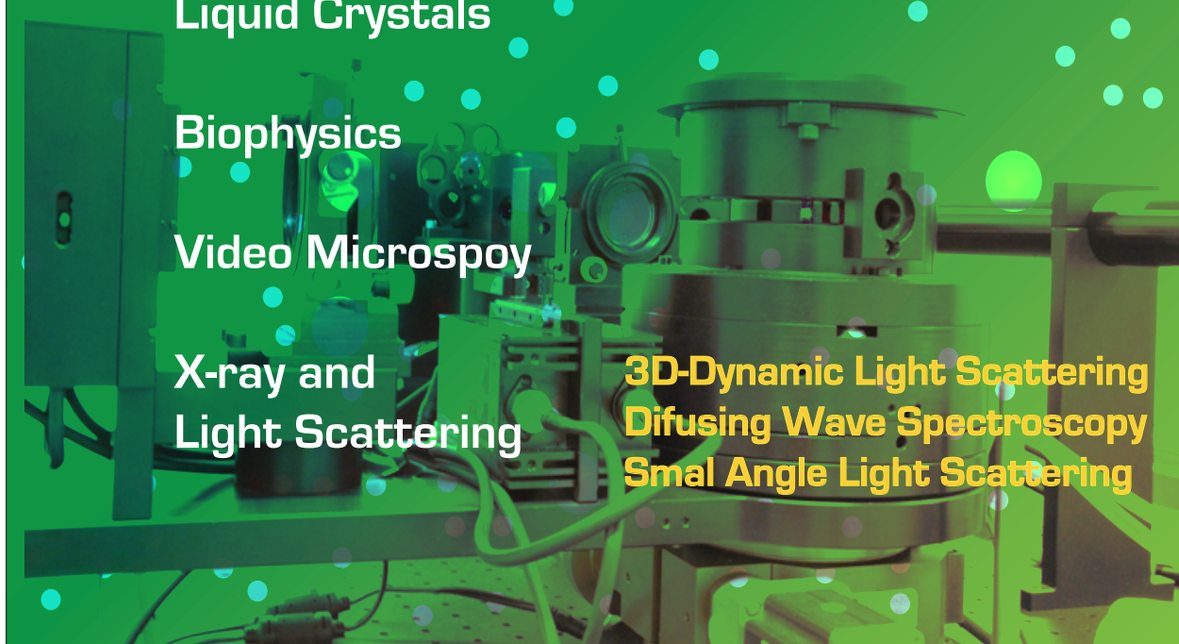
Liquid Crystals

Biophysics

Video Microspoy

X-ray and Light Scattering

3D-Dynamic Light Scattering
Difusing Wave Spectroscopy
Smal Angle Light Scattering



Group members:

Pedro González Mozuelos
José Miguel Méndez Alcaraz
Mauricio Carbajal Tinoco
Martín Hernández Contreras
Luis Fernando Rojas Ochoa

Studentss:

Adriana Campos-Ramirez
Brisa Lizath Arenas
Cesar Alejandro-Baez
Fernando Favela
Gualberto Ojeda-Mendoza
Liliana Toscano-Flores
Oscar Taxilaga-Zetina

www.cinvestav.mx

Center for Research and Advanced Studies of the National Polytechnic Institute

Dr. Kitchens Research Group: **Metal and Cellulose Nanoparticle Synthesis and Surface Chemistry Modification**

Various synthesis techniques

- AOT reverse micelle
- Brust
- Direct reduction in aqueous media
- Acid Hydrolysis

Size Selectivity

- Gas Expanded Liquids, GXL
- Varying concentration of stabilizing ligand

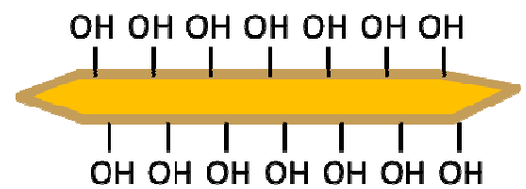
Surface Chemistries

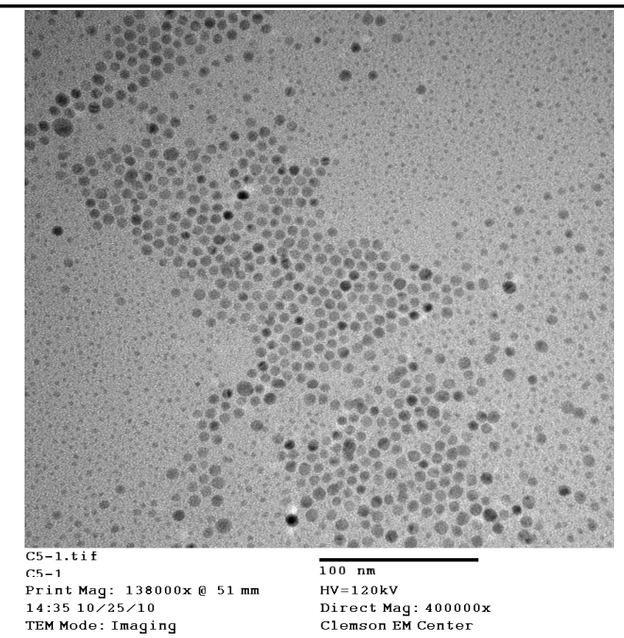
- Cationic surface charge
- ATRP

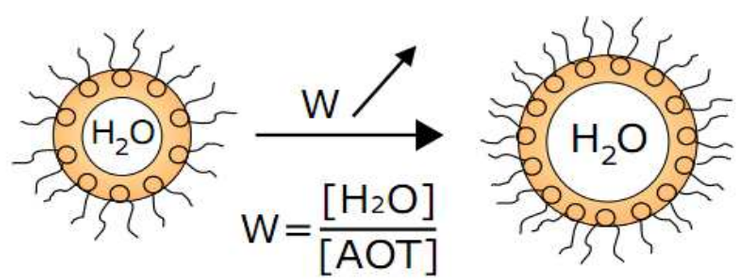
Ligand-solvent Interactions

- SANS

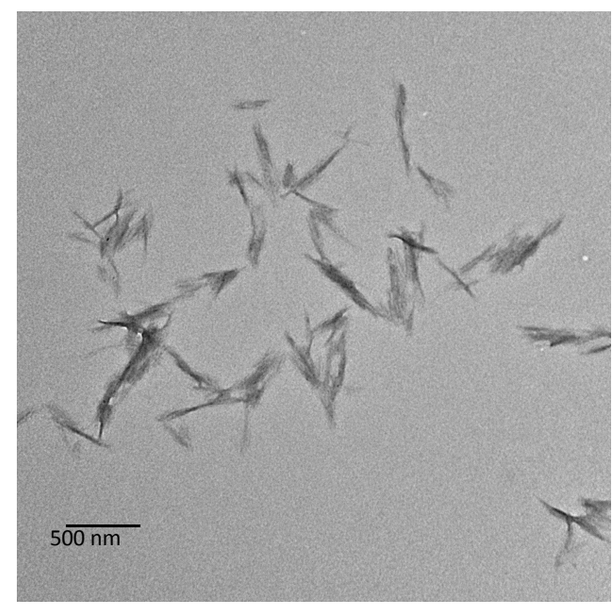
Cellulose Nanocrystal, CNC







Water amount ⟶ size of the micelles



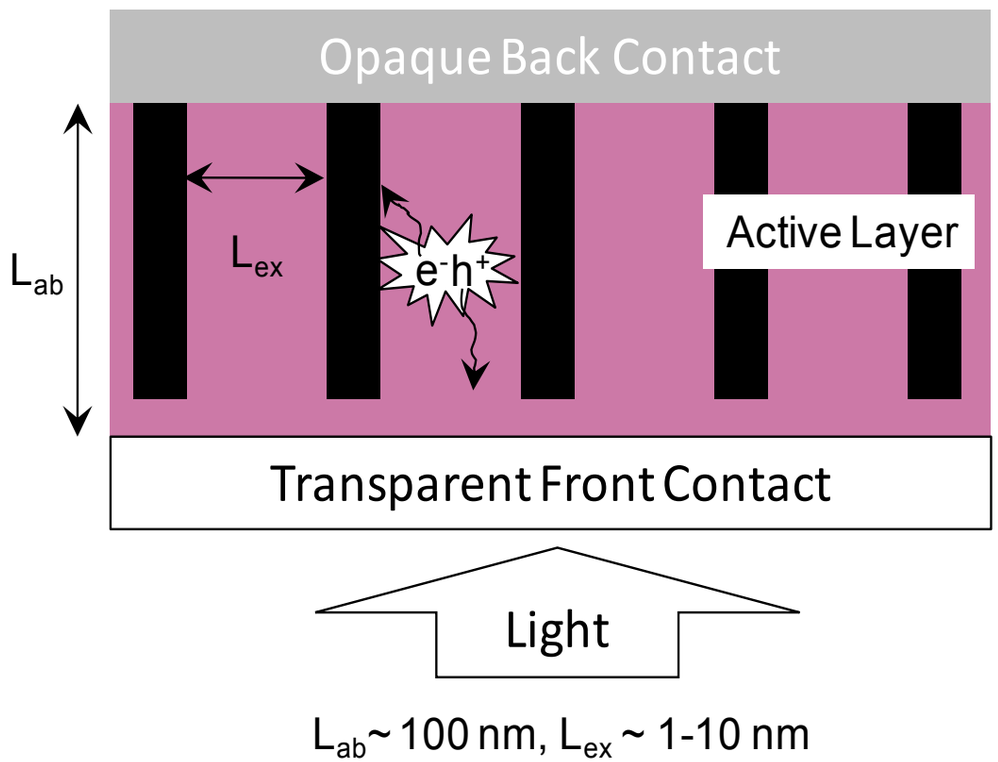
Mekonnen Lemma Dechassa
Postdoctoral fellow (Luger Lab)
Colorado State University Department
of Biochemistry and Molecular Biology
Fort Collins, Colorado

Research Interest: Chromatin Structure and Dynamics
Structural biology of the centromere chromatin: centromere nucleosome assembly mechanism and structure of centromeric chromatin

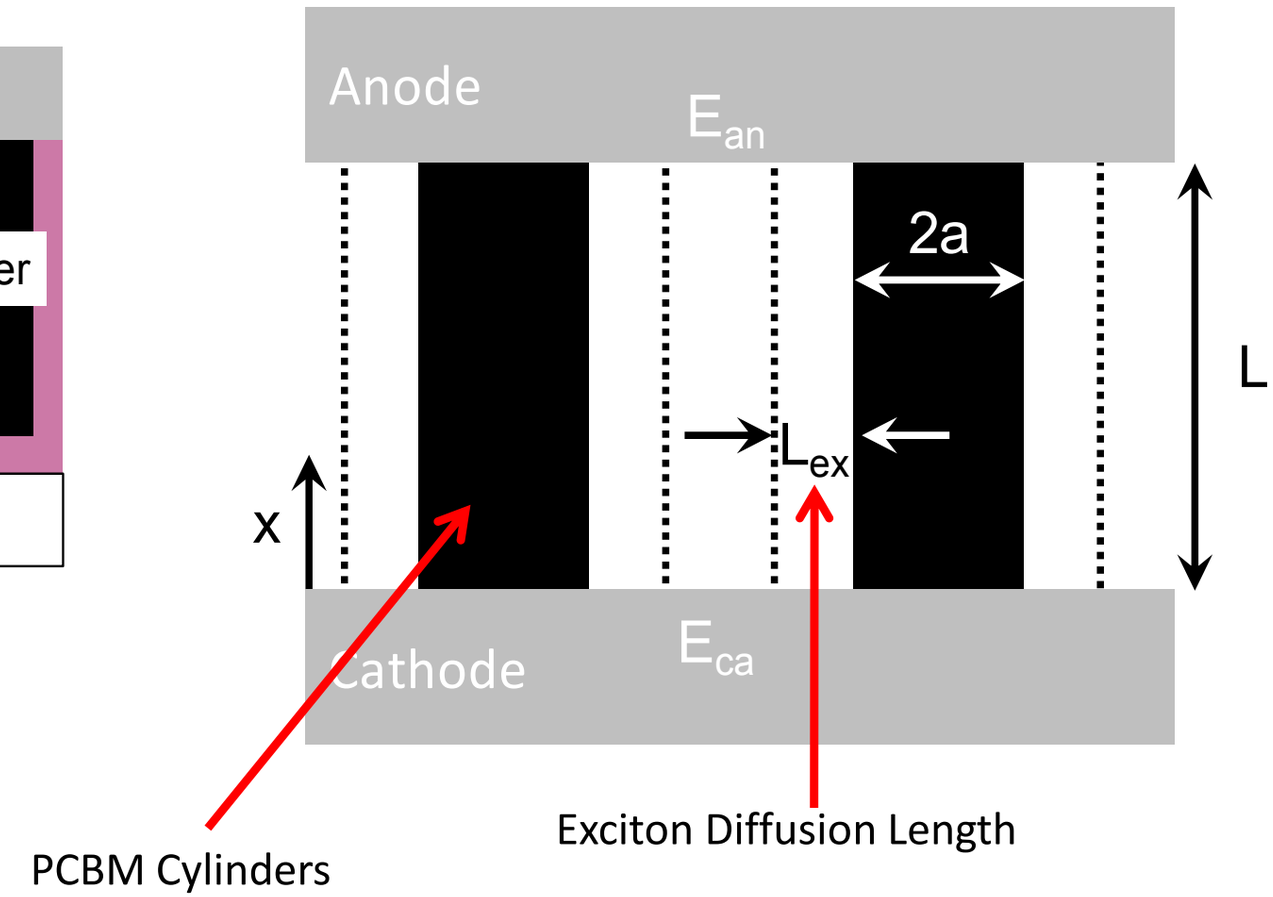
Tao Yu

Understanding and Improving Electron Extraction from the Organic Layer into the Back Contact

Comb Structure: Ideal Solar Cell Structure



Morphological Model of the Solar Cell



Characterization: Small angle neutron scattering and reflectivity will be performed to obtain a concentration profile and analyze the phase separated region.

Goal: The overall goal is to understand the nature of the interface between the active layer and the back contact. Additionally, we will investigate the influence of regional morphology on device performance.

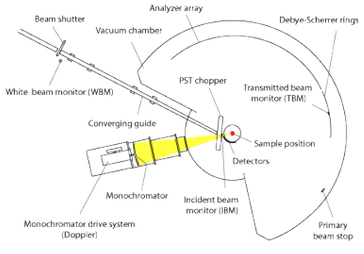
The project is a collaboration between Michael Mackay at (UD) and Derrick Swinton at (LU)

QENS Measurement of Low-Temperature dynamics in Protein Hydration Water

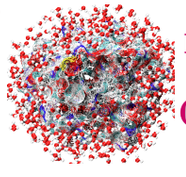
Introduction

High pressure denatures most of the proteins at room temperature. At the same time, for a protein at ambient pressure, it loses its biological activities and becomes less flexible below a characteristic low temperature (about 220 K). What will happen while protein is subjected to high pressures and low temperatures simultaneously? Would it become less flexible? We discover that hydrated proteins will remain active and biologically functional at lower temperatures under moderate pressures. Here we use a term "soft" or "hard" to describe the protein flexibility. Contrary to the intuition that proteins will become harder under the compression, they actually become softer under pressure at low temperatures. This dynamic behaviour of hydrated protein may be triggered by the anomalous behaviour of its hydration water at low temperatures.

QENS Experiment

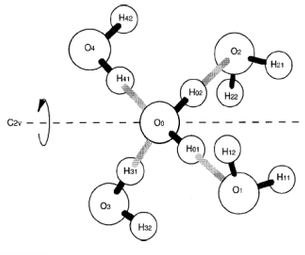


Quasi-elastic Neutron Scattering (QENS) experiments were performed at NG2 in the NIST Center for Neutron Research (NCNR).



Protein Sample: Lysozyme (Hen Egg White)

Relaxing Cage Model

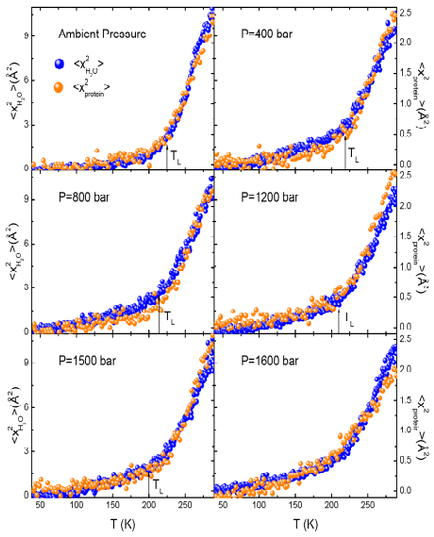


At supercooled temperatures, a water molecule is confined in the cage formed by its neighbors through H-bonds.

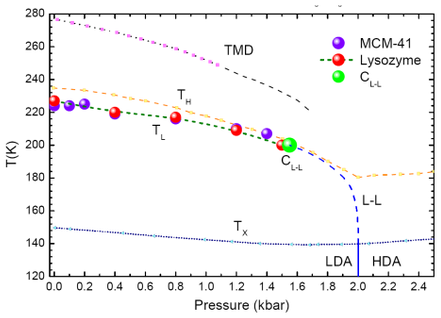
For *short times* it performs harmonic oscillations and vibrations inside the cage.

For *longer times*, the cage begins to relax and the molecule escapes (α-relaxation).

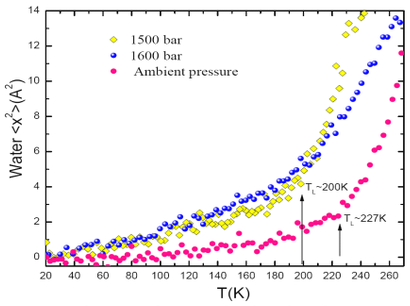
Results



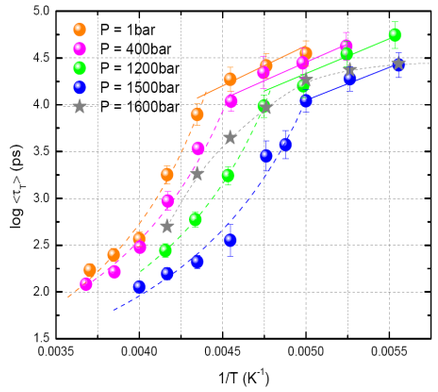
MSD, the degree of "softness" of the protein, shows that the protein undergoes a pressure dependent crossover following its hydration water.



Comparison of MSD of protein hydration water under different pressures.



Comparison of protein hydration water and super-cooled confined water in temperature-pressure phase diagram.



Pressure dependence of the average translational relaxation time of protein hydration water.

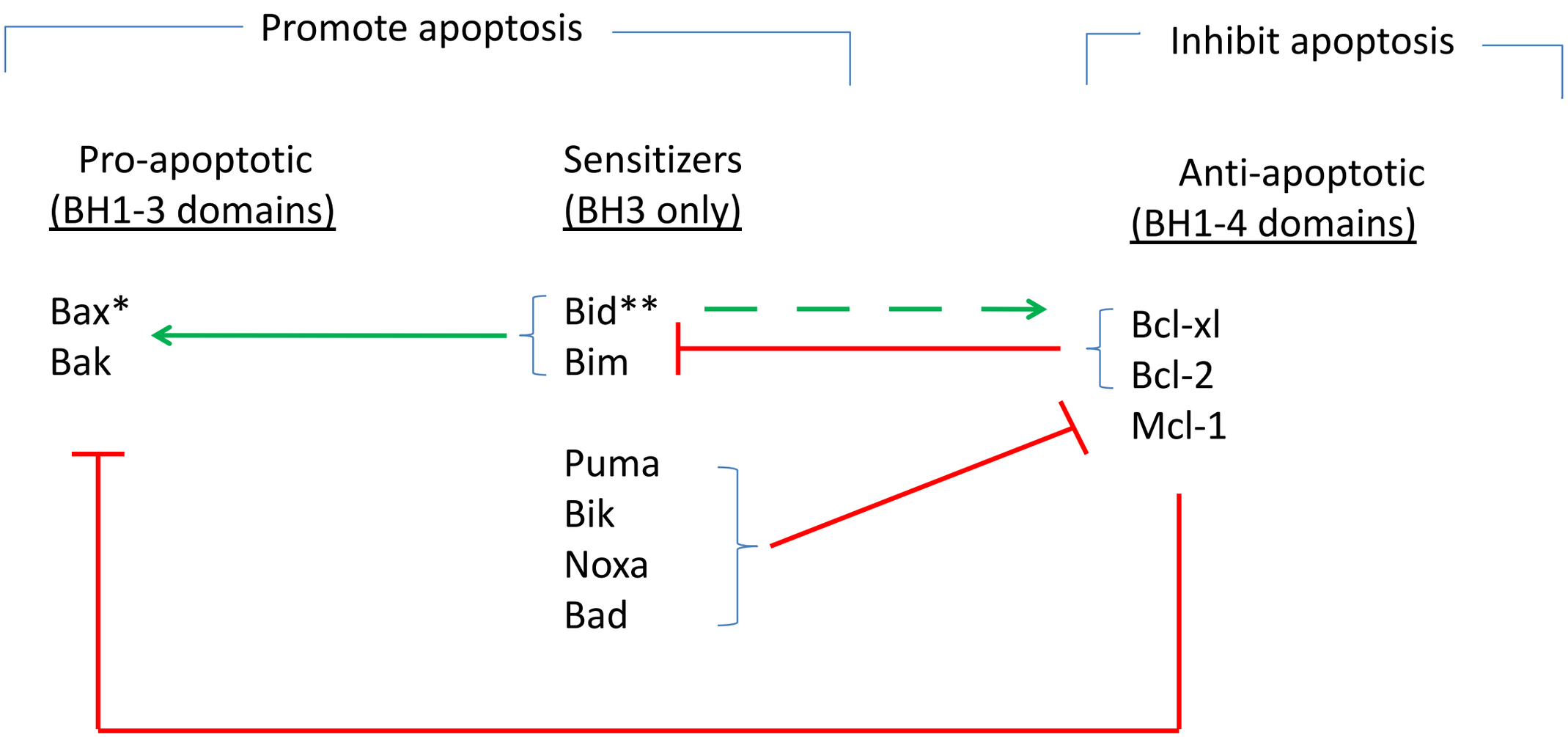
Conclusions

1. We observe that hydrated proteins remain soft and biologically functional at lower temperatures under pressures.
2. In our measured low temperature region, increasing the pressure up to 1500 bar can have the same effect on the relaxation time as increasing the temperature.This phenomenon may be rationalized from the point of view of the existence of the second liquid-liquid critical point in the protein hydration water in the super-cooled region.

Bcl-2 family of proteins

Apoptosis : form of self mediated cell death

Failure can result in uncontrolled proliferation of harmful cells (cancer).



Migration from polymer-nanoclay films: method development, validation and modelling

Yining Xia, School of Packaging, Michigan State University, East Lansing, MI 48824

Part 1

- **Background of nanocompoments in food packaging**

- *Applications*
- *Migration and health risks*
- *Regulations*

Part 2

- **Characterization of nanocomponents alone and in solvent**

- *Size and size distribution*
- *Aggregation and dispersion*
- *Concentration*

Part 3

- **Incorporation of nanocomponents into polymers**

- *Compounding of polymer-nanocomp. blends*
- *Processing of polymer-nanocomp. films*
- *Characterization of the films*

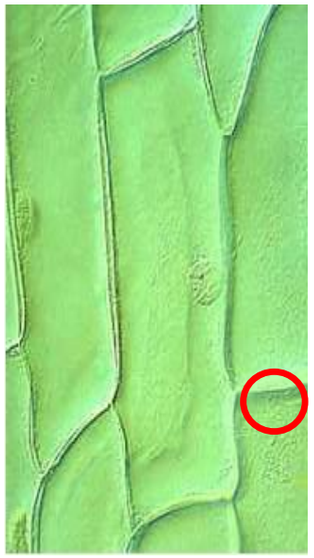
Part 4

- **Migration testing and modelling**

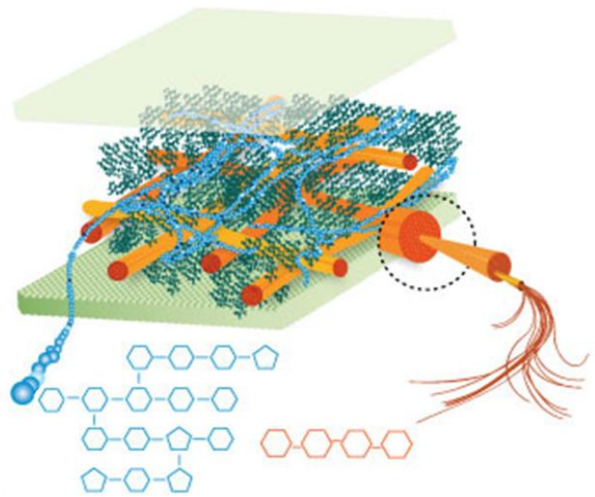
- *One-sided and two-sided migration testing*
- *Models development and validation*
- *Effects of migration on the films*

Nanostructure of Primary Plant Cell Wall

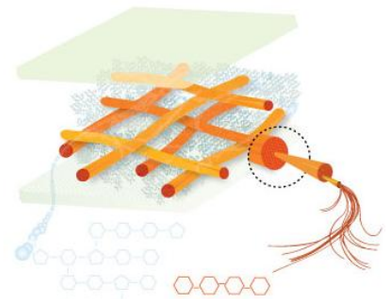
PENNSTATE 1855
Shih-Chun Huang
Dr. Janna Maranas

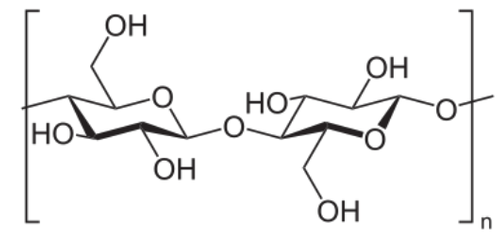


Primary Plant Cell Wall

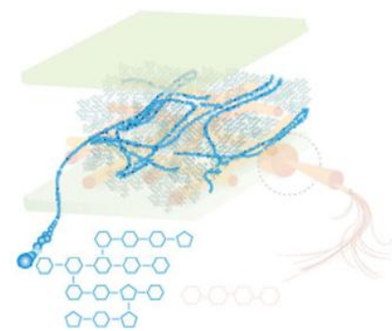


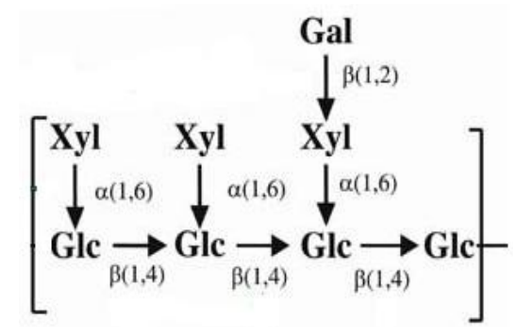
Cellulose microfibril: Ordered chain and disordered chain



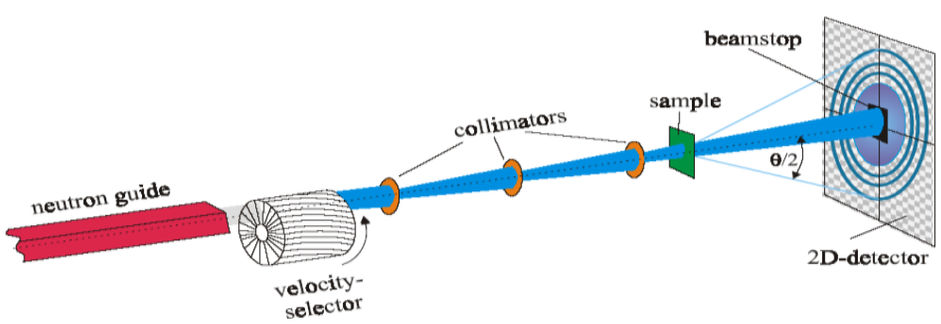


Hemicellulose: Supportive network

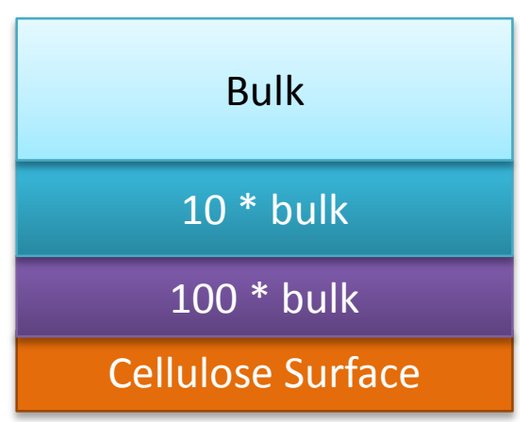


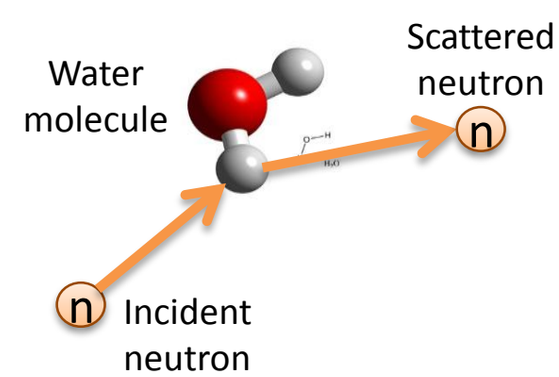


SANS → System structure information



QENS → Water dynamic information





TEMPLE UNIVERSITY Dr. Rongjia Tao`s Research

Rheology For Efficient Energy Production and Conservation rheology

Electric Field Magnetic field =>crude oil (35%)

Electric Field => Diesel (20%)

Magnetic field => blood viscosity (30%)

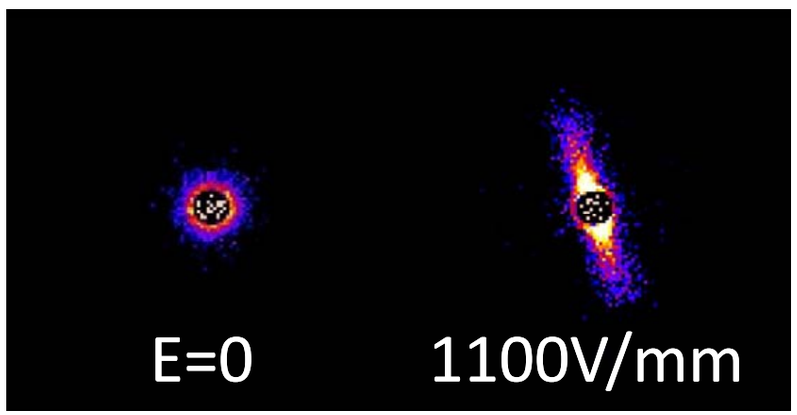
Crude oil => Pipeline Transportation (cold area/off short)

Oil san => Deep Oil Well

Fuel injector

Health?

Food?



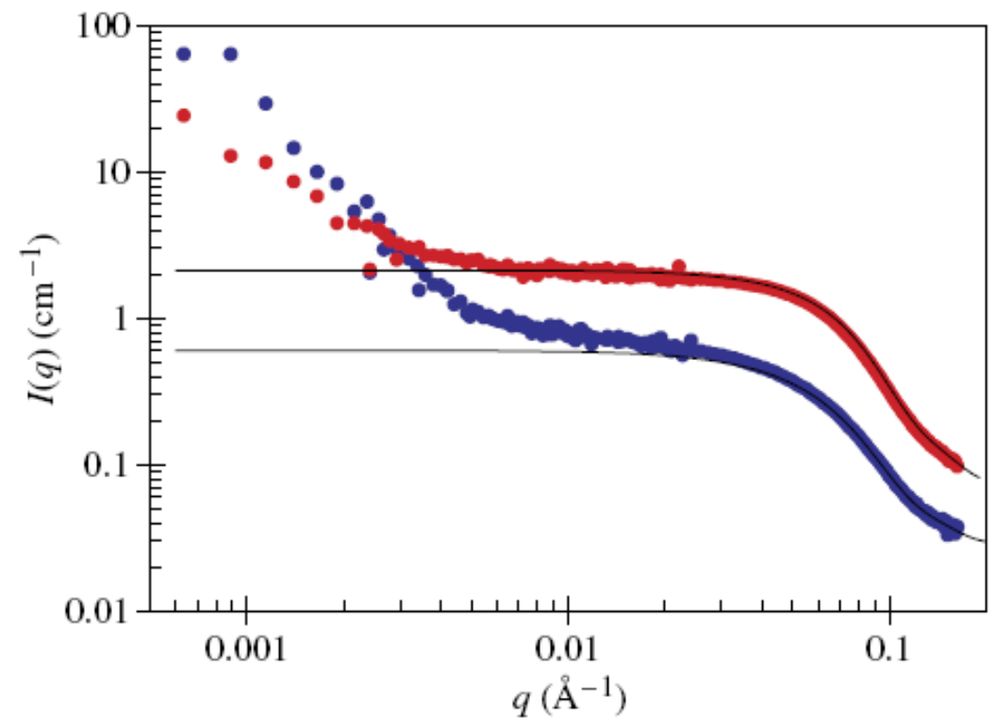
Protein Aggregation

Maria Monica Castellanos

- Aggregation limits the efficacy and shelf life of protein therapeutics and causes a numerous disease states.

- Experimental evidence:
  - Increase of viscosity at low shear rates.
  - Upturn in scattering at low q (peaks for protein interactions).

- Simulations to study protein interactions and compare with experiments.



SANS data on BSA in D2O with PBS at 25 °C. Data for two BSA concentrations: for synovial fluid (11 mg/mL, dark blue) and for blood (44 mg/mL, red). Solid curves are the form factors of BSA calculated.

Taken from: Oates, K. M. N., Krause, W. E., Jones R.L. and Colby, R. H. J. R. Soc. Interface (2006), 3, 167-174.

Michigan Chemical Engineering: Dr. Fogler's Research Group

- Funded entirely by industrial sponsors
- Research areas:
  - Paraffin deposition
  - Asphaltene deposition and precipitation**
  - Scale deposition
- Asphaltenes are a crude oil fraction that form aggregates/nanoparticles in solution
  - I use SANS and SAXS to study asphaltene structure and behavior

Microstructure evolution in Catanionic Surfactant mixtures

Hari Katepalli, Arijit Bose

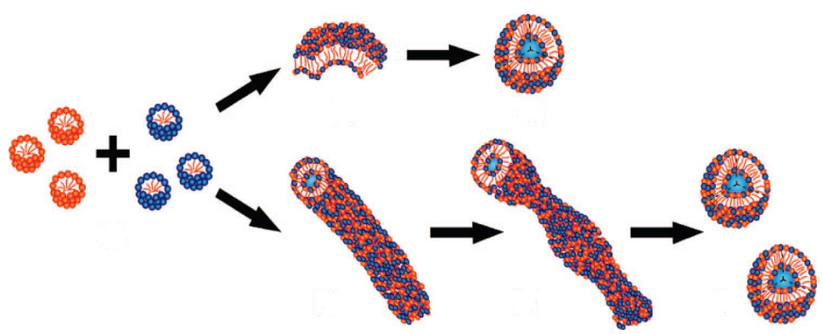
Department of Chemical Engineering, University of Rhode Island, Kingston, RI 02881

Motivation:

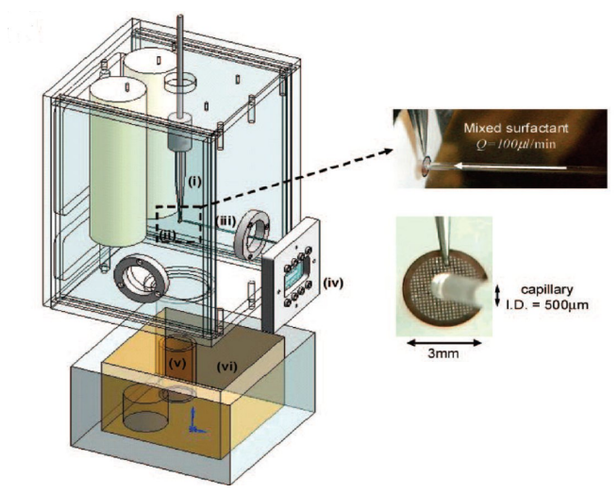
To test a hypothesis that a balance between line and bending energy critically impacts structures and dynamics in the micelle to vesicle transition.
Understand the principles that govern evolution dynamics in surfactant systems.
Finding ways to control these transitions

Approach:

Using different surfactant systems based on their expected line and bending energies.
Use micro fluidics to control residence times and mixing conditions.
Image using time resolved cryogenic transmission electron microscopy



Different routes for surfactant self-assembly



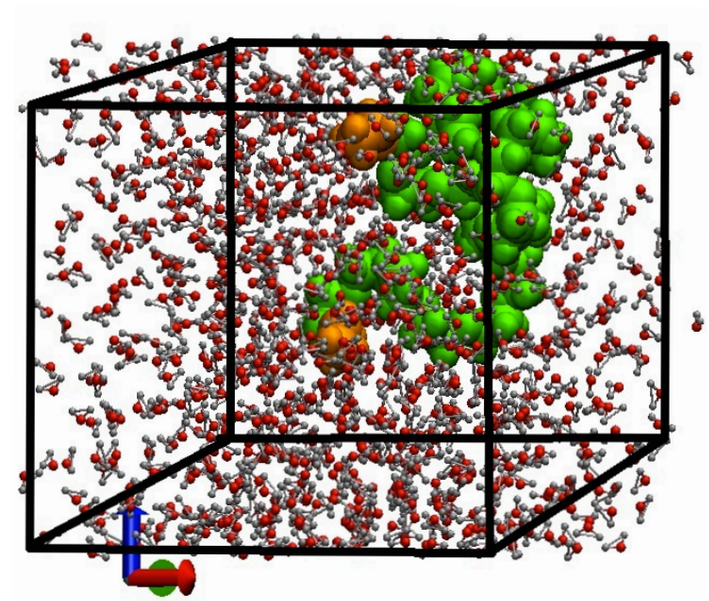
CEVS integrated with micro-fluidic chip for making sample for Cryo-TEM

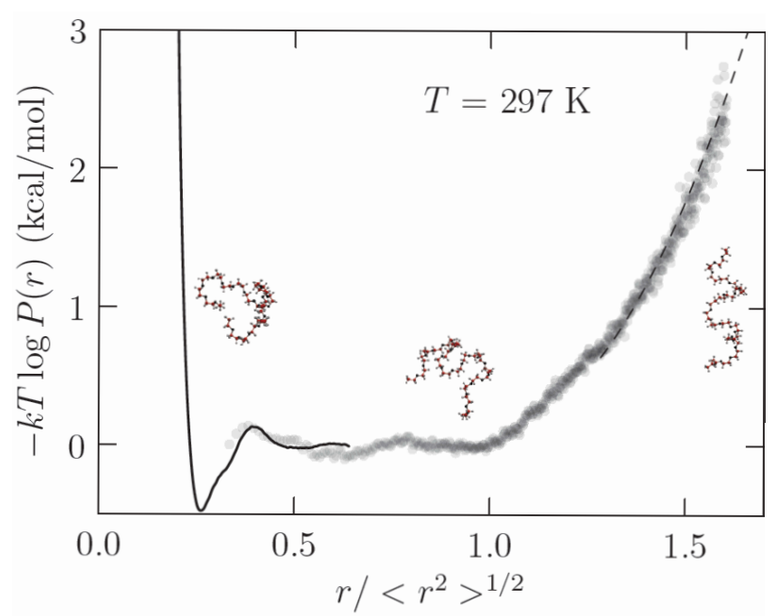
Financial support: National Science Foundation; Collaboration – Dr. Tripathi group, Brown University

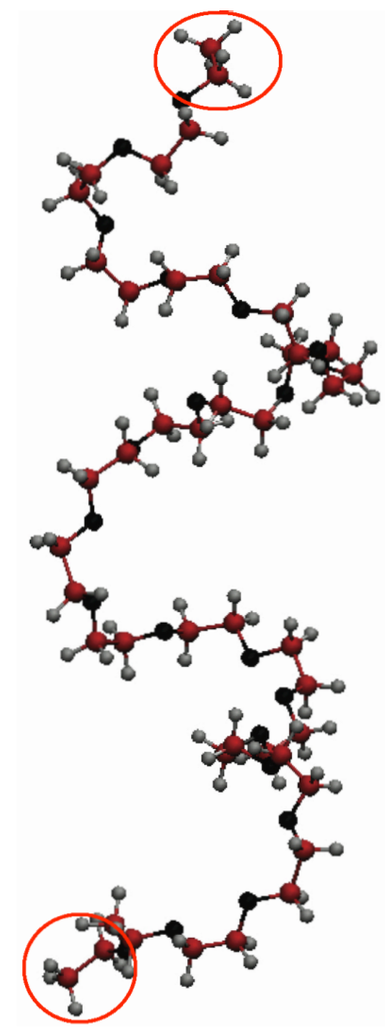
Molecular Simulations to Study Thermodynamics of $(-CH_2-CH_2-O-)_n$ Solutions

Mangesh I. Chaudhari, Lawrence Pratt
Tulane University, New Orleans, LA, 70118

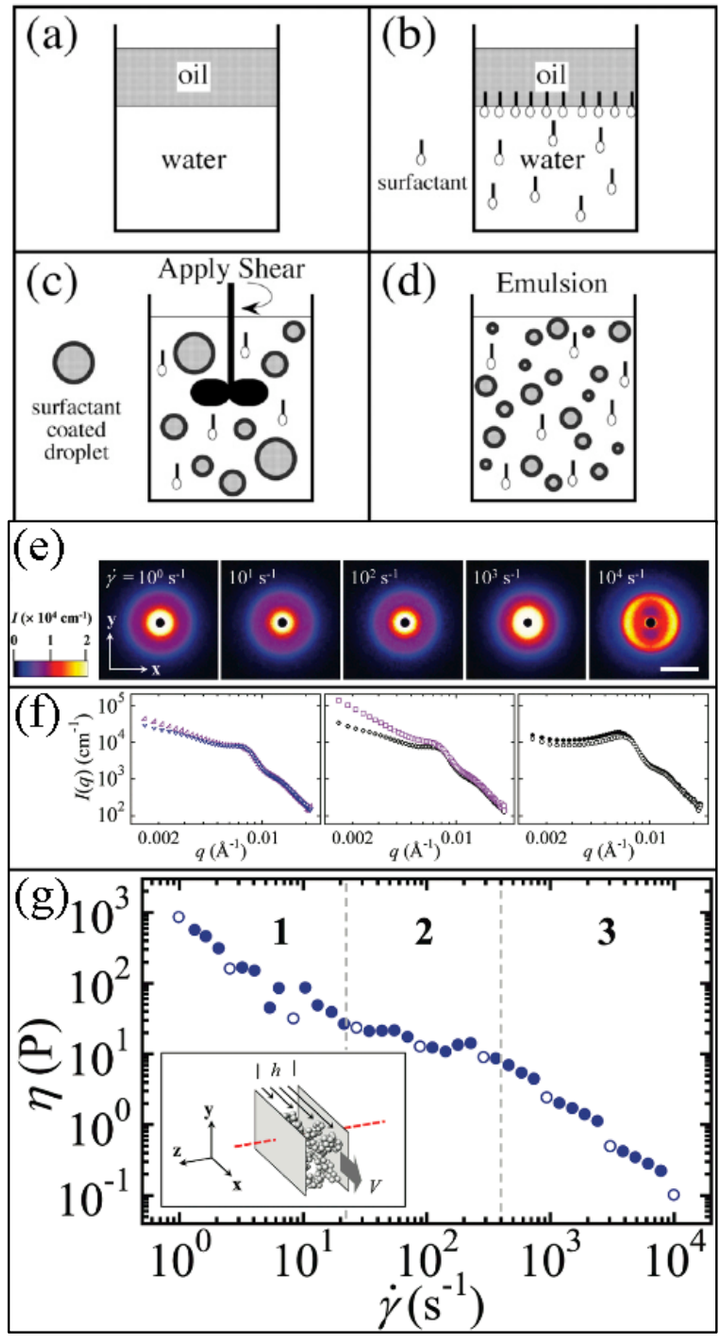
- Polyethylene Oxide polymers are intrinsic to oil spill dispersants and need efficient thermophysical modeling to facilitate comparison between lab-scale, field-scale, and ocean-scale results.
- Molecular simulations are done on these polymers to understand their thermodynamic properties in solutions
- Direct measurement of polymer and solvation structure is essential for such modeling and require X-ray or neutron diffraction studies of these polymer solutions
- One of the simulation result for atom pair correlation is shown here and we want to confirm it with diffraction experiments and subsequently include these results in available extended Flory Huggins model

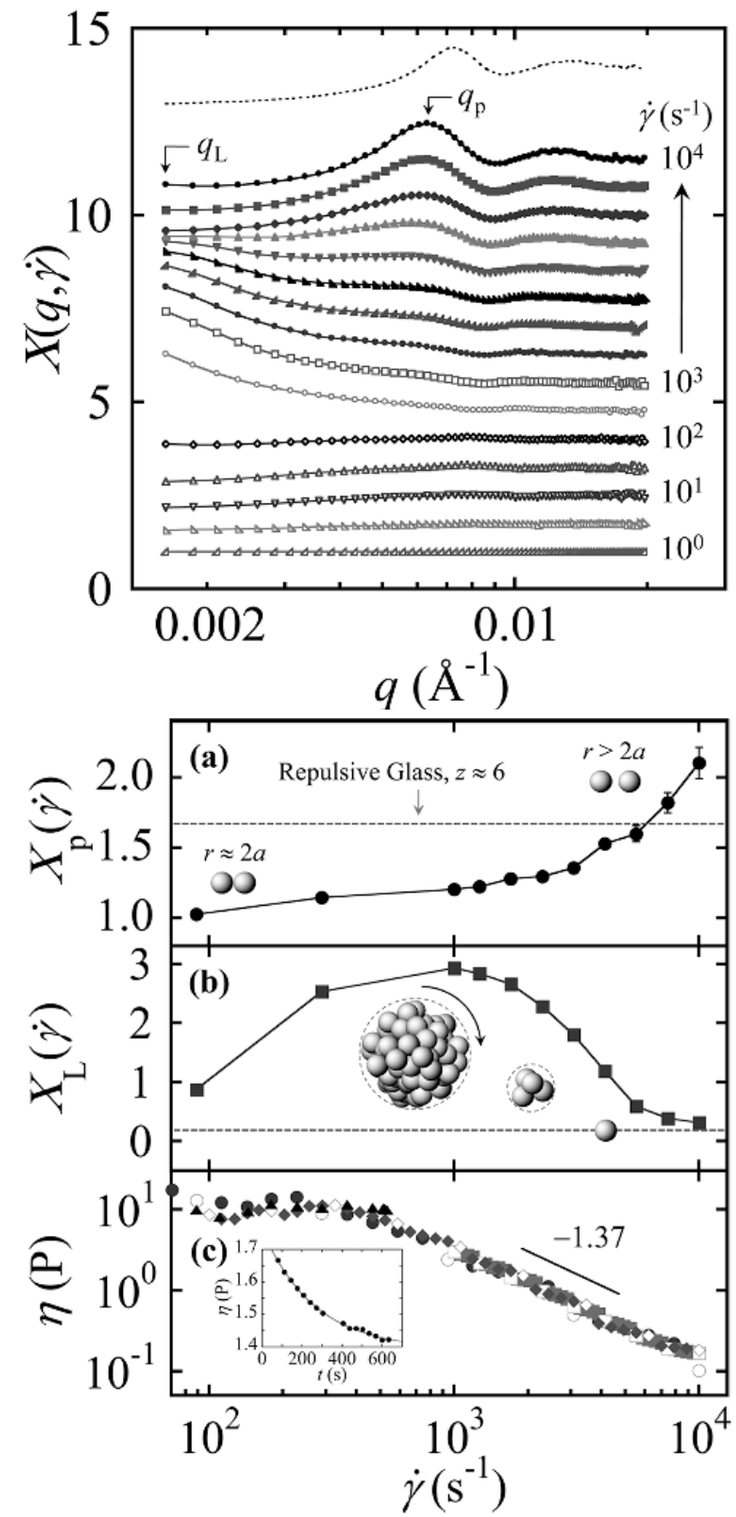






Shear Induced Disruption of Nanoemulsion





Mason, T.G., et al., *J. Phys.: Condens. Matter* 2006;
Wilking, J.N., *et al.*, *Langmuire*, 2011

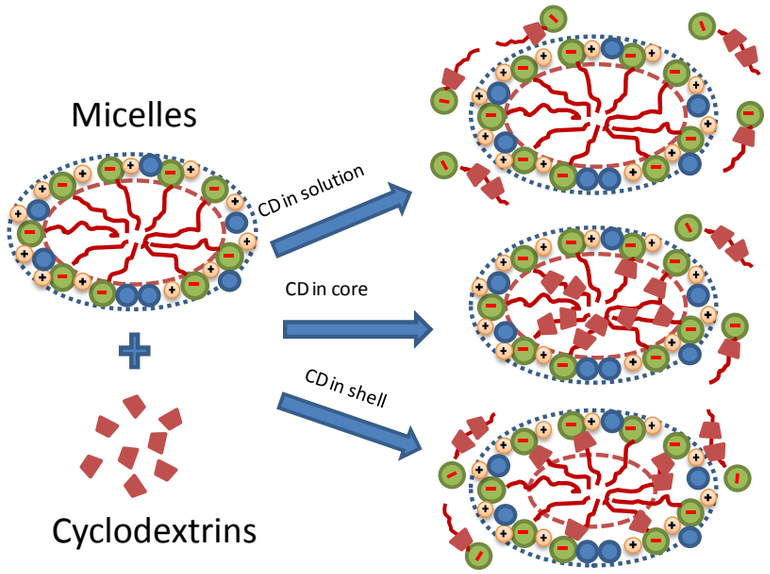
University at Buffalo The State University of New York

Directed Macromolecular Assembly in Solution and at Surfaces

Ankitkumar Fajalia and Marina Tsianou
Department of Chemical and Biological Engineering, University at Buffalo

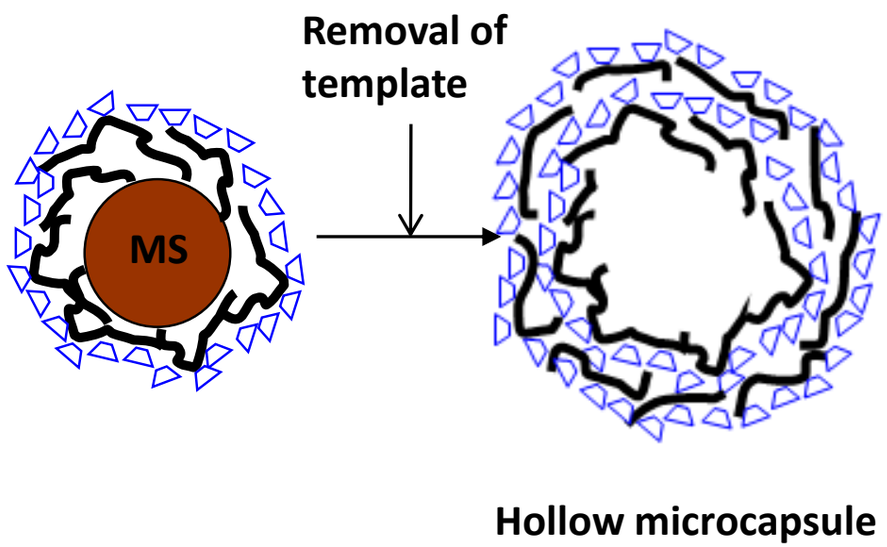
Surfactant micelle formation and disruption under different conditions and environments

- Objective: How do cyclodextrins affect the micelle structure and the interactions between them?
- System
  - Surfactants: sodium dodecyl sulfate(SDS), Aerosol-OT
  - Cyclodextrins (α- or hydroxypropyl β-CDs)
- Characterization Technique
  - Small angle neutron scattering
    (Contrast matching with deuterated surfactant)



Structure and conformational changes of interpolyelectrolyte complexes in aqueous media or at surfaces (layer-by-layer films)

- System
  - Polyelectrolytes
  - Cyclodextrins (sulfonated β-CDs)
  - Templates: glass slide, mesoporous silica(MS)
- Characterization Techniques to be used
  - Small angle X-ray scattering
  - Neutron reflectometry
  - SEM, DLS, AFM, FTIR, TGA, UV spectroscopy



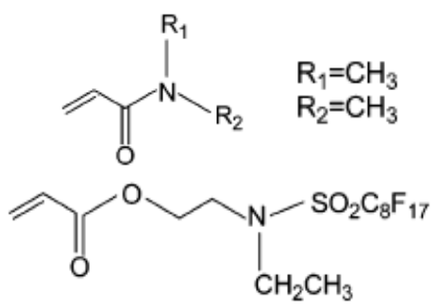
Jinkun Hao

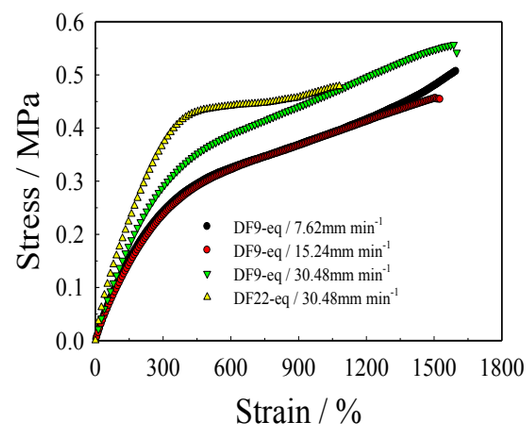
Advisor: **Robert A. Weiss**

Current Research Projects in R. A. Weiss's Group

❑ Hydrogels

- Hydrophobically Modified Hydrogels
- Double Network Hydrogels

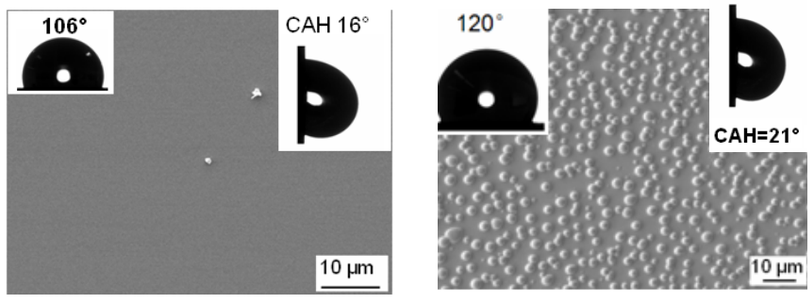




IONOMERS

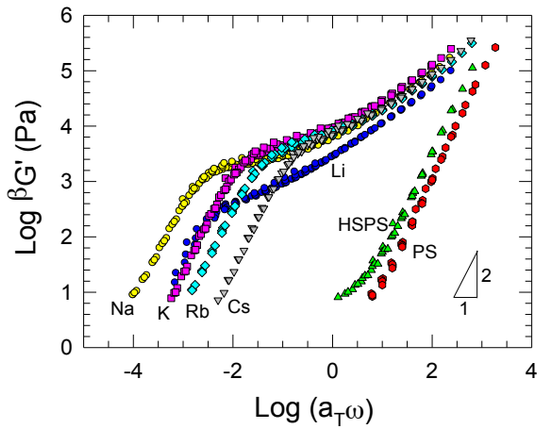
❑ Controlled Surface Microstructure

2.6Li-SPS (M ~ 4 kg/mol)



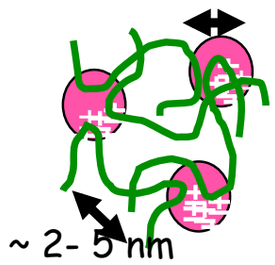
❑ Rheology of Ionomers

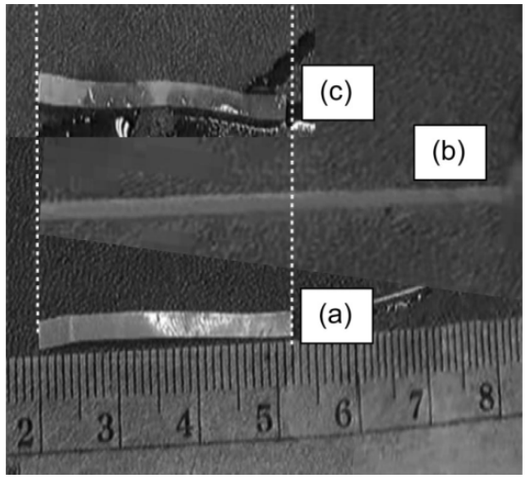
SPS: 4kg/mol (unentangled melts)



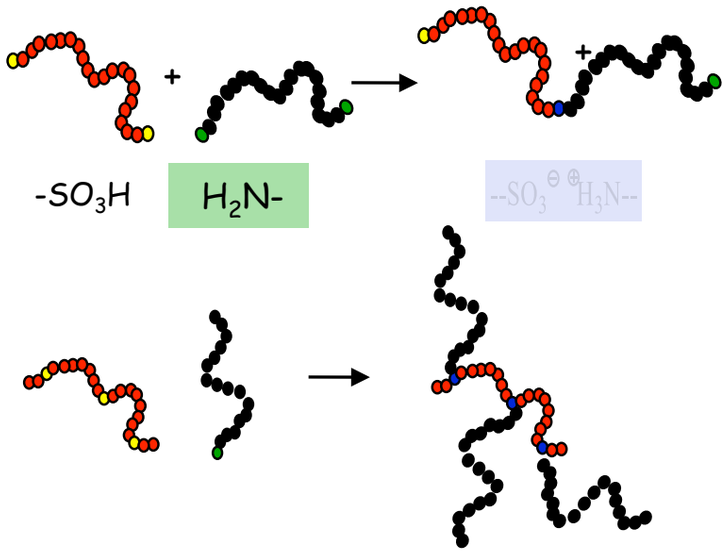
❑ Shape Memory Polymers

Zn-SEPDM containing 33.3wt % ZnSt





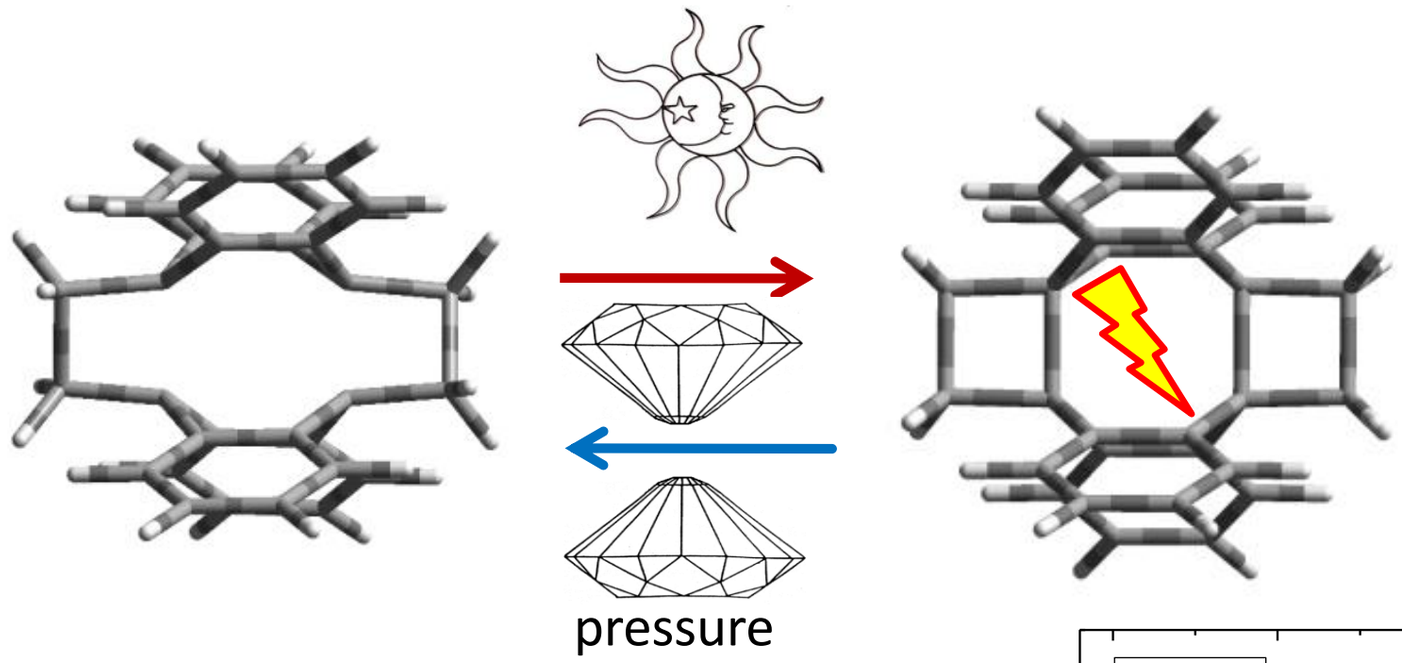
❑ Supramolecular Polymers

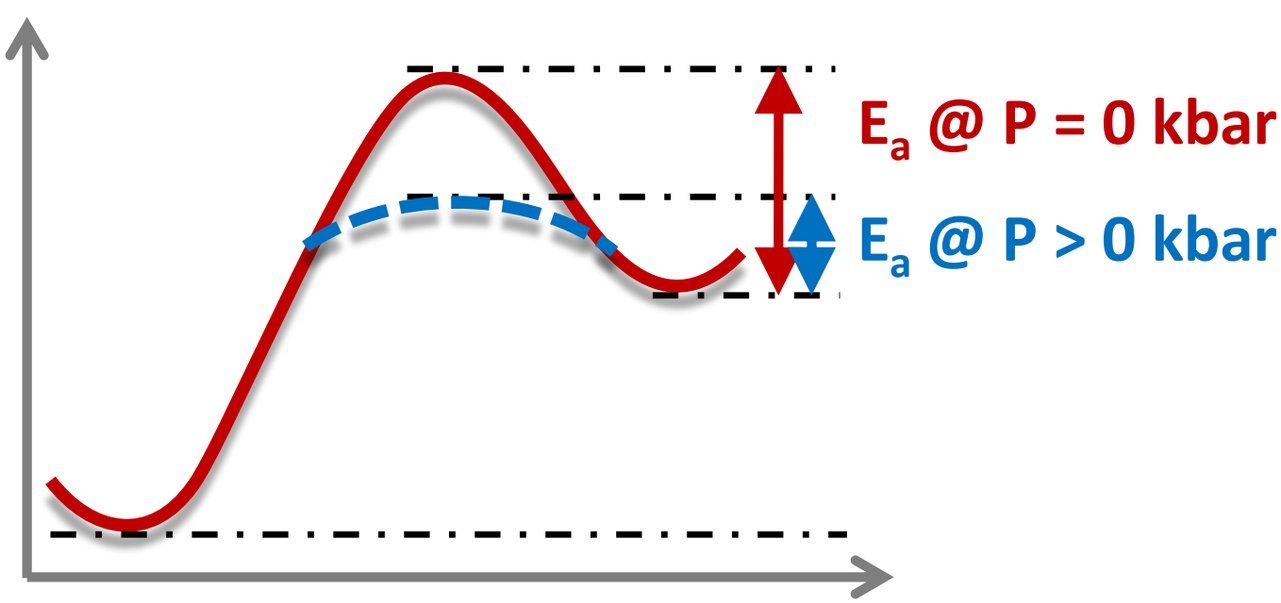


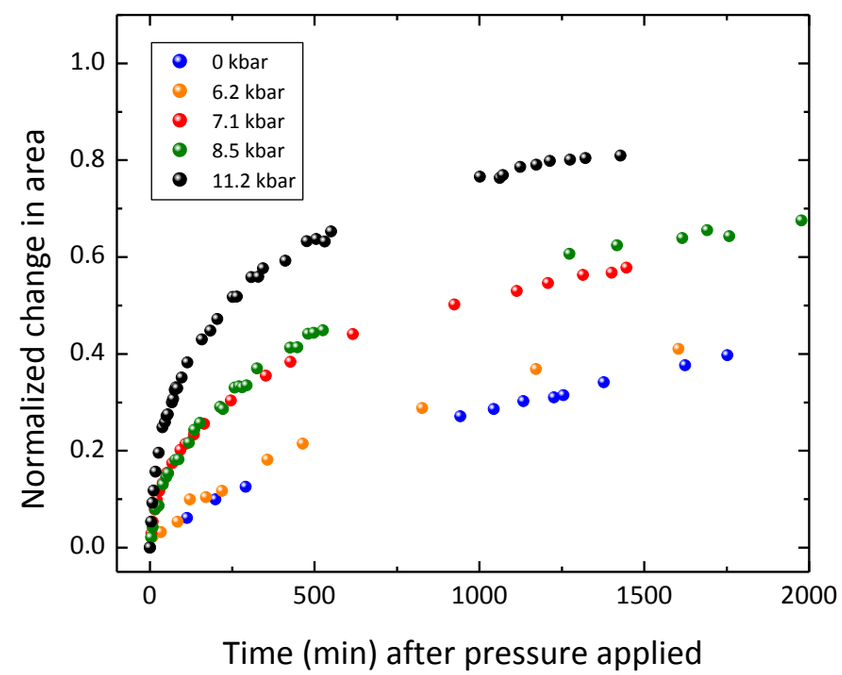
Mechanochemistry and Molecular Engineering

Sebastian Jezowski

Application of mechanical force to selectively break or form a covalent bond



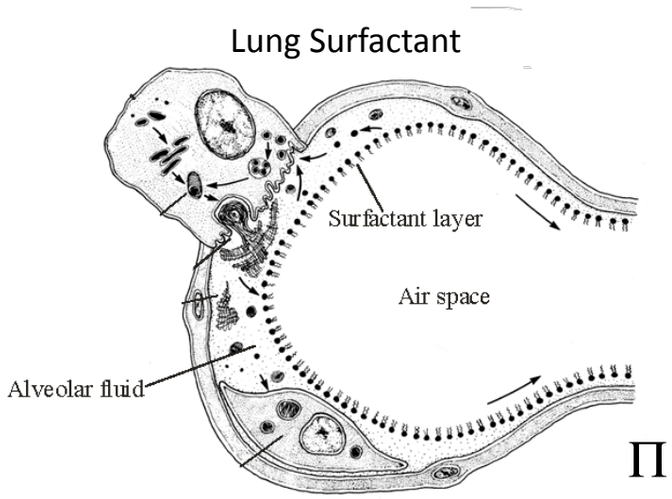




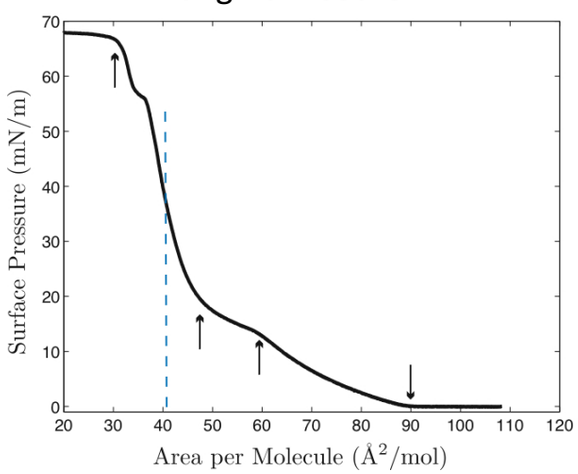
Lee Lab Research

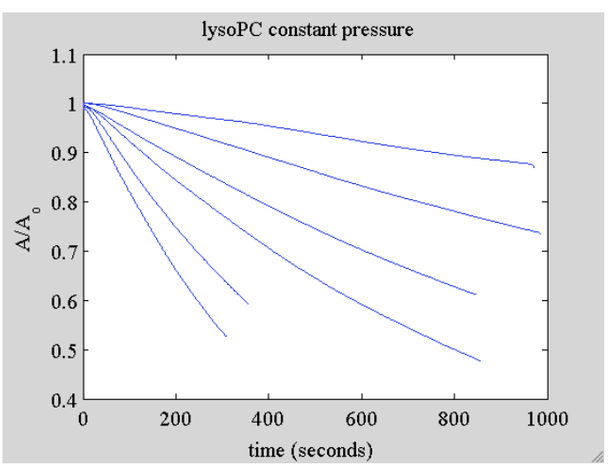
Charles Heffern
University of Chicago

Lung Surfactant

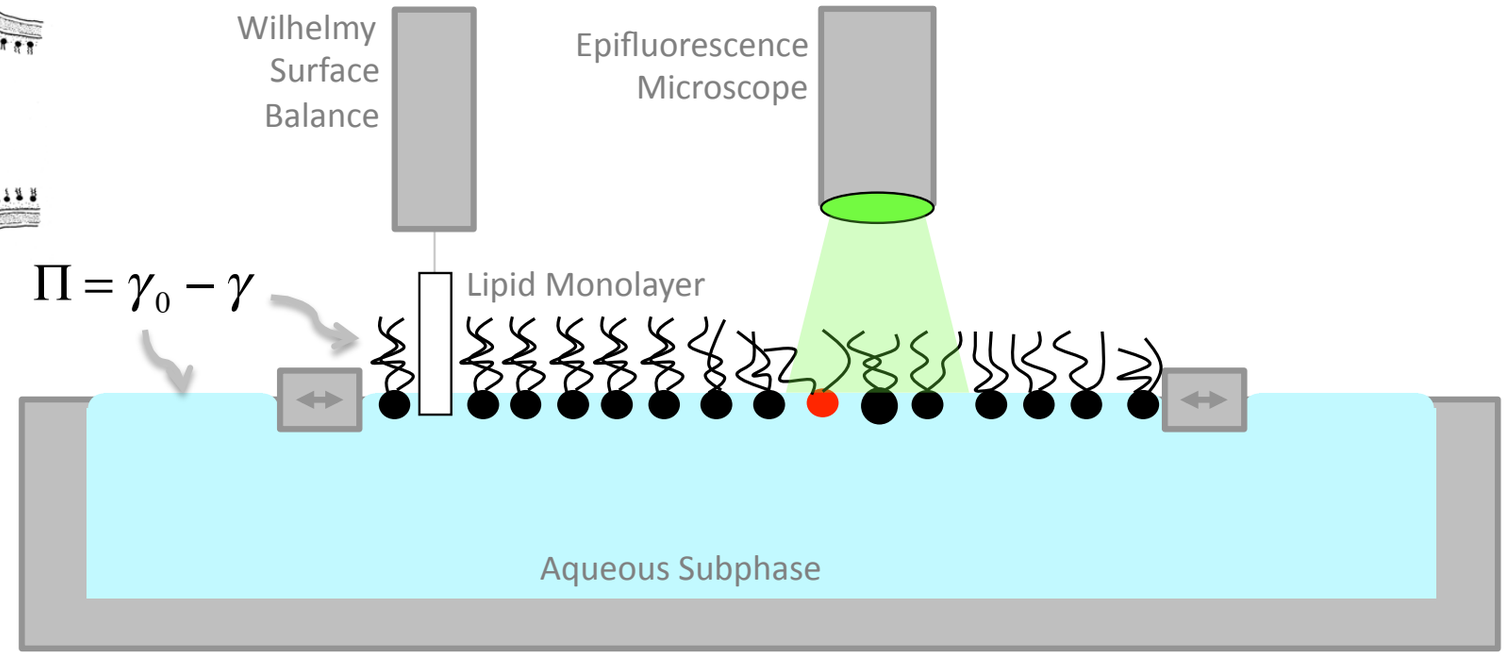


Langmuir Isotherm

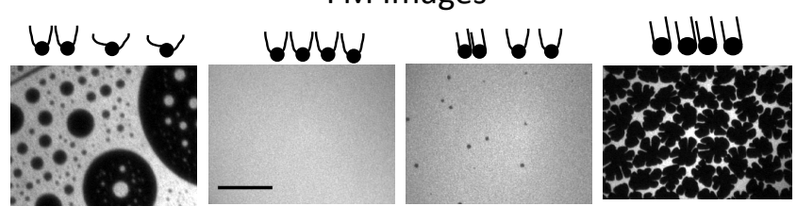




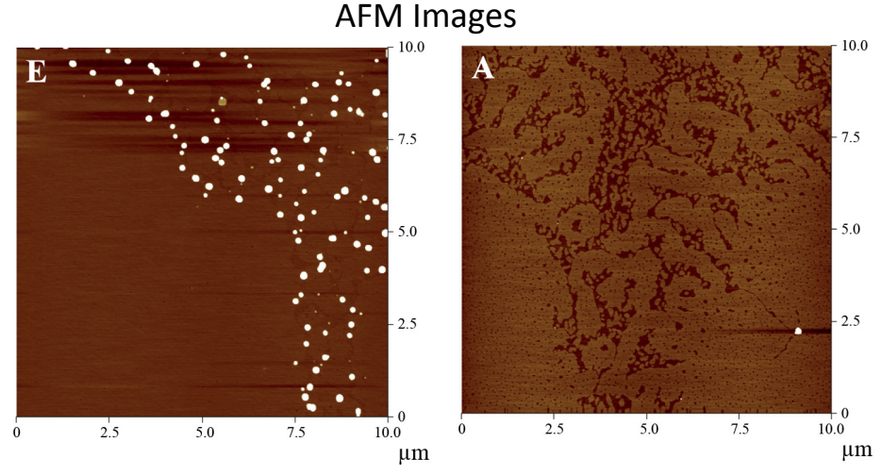
$$\Pi = \gamma_0 - \gamma$$

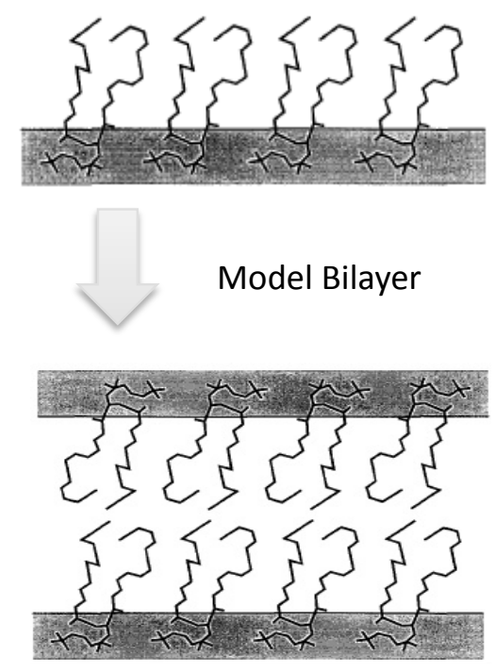


FM Images



AFM Images



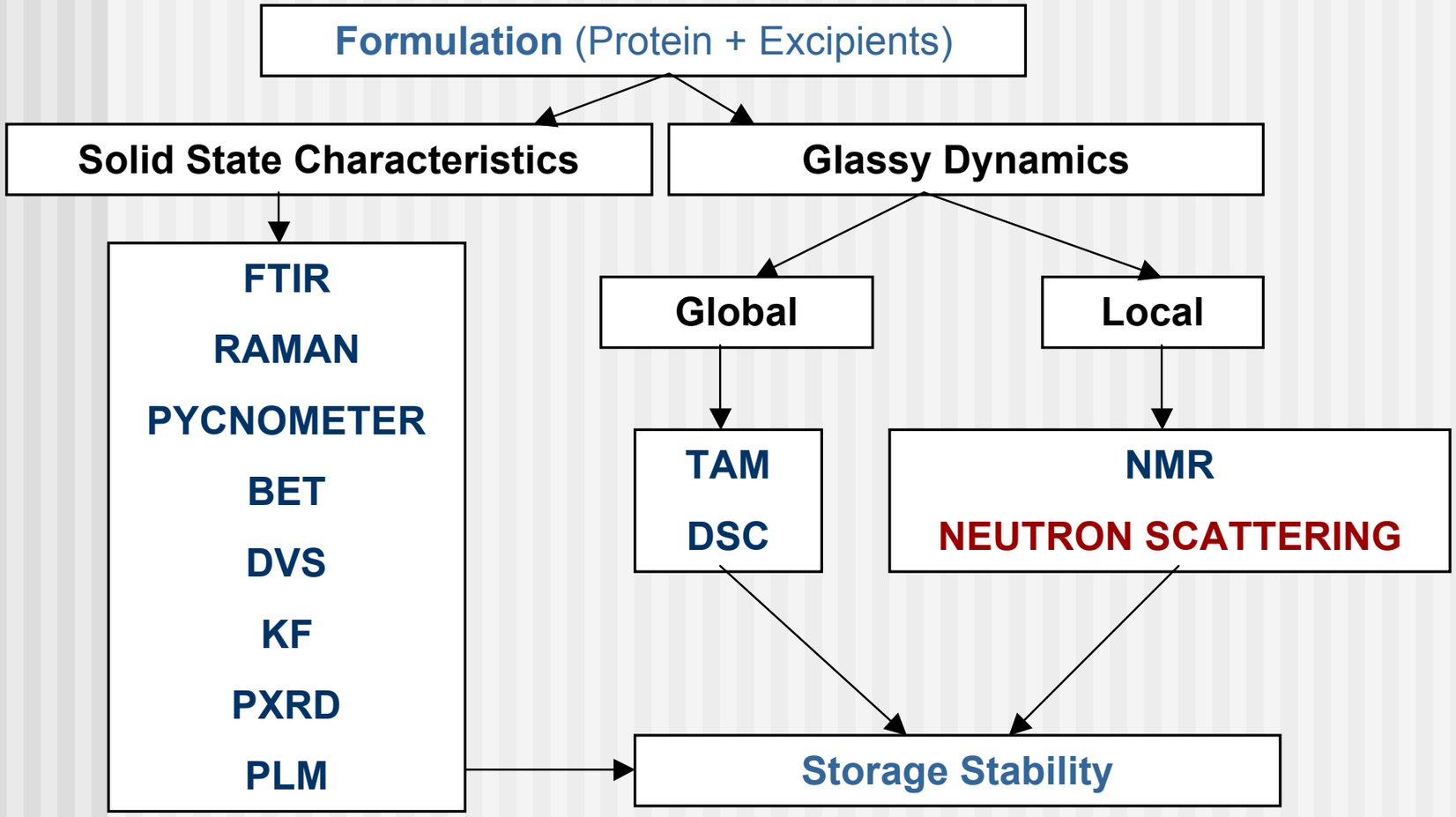


Model Bilayer

Pikal Laboratory
University of Connecticut

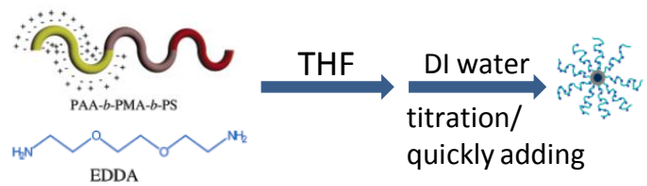
Grad Students: Kelly Forney, Pooja Sane, Mary Kleppe
Post Docs: Puneet Sharma, Loren Schieber, Meena Thakur, Kristyn Greco
Visiting Scientist: Hiroshika Goshima

- **Lyophilization of Proteins and Pharmaceuticals**
  - **Process and Formulation**
- **Formulation - Impact on Storage Stability**

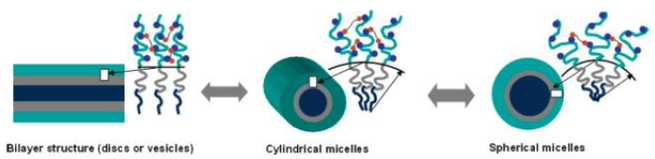


Hierarchical self-assembly of block copolymer and peptide via kinetic control

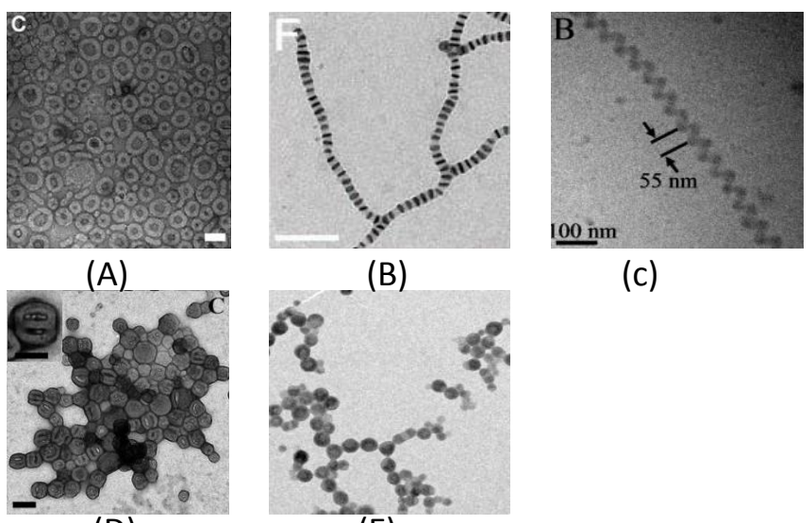
Darrin J Pochan Group



Scheme of self-assembly of triblock copolymer



higher interfacial curvature is preferred at higher water content

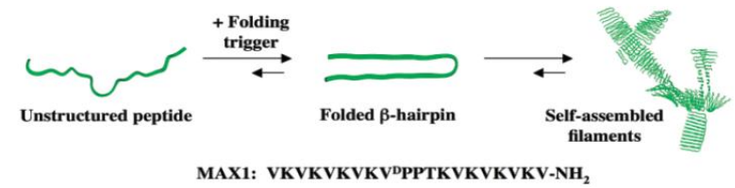


(A) (B) (c)

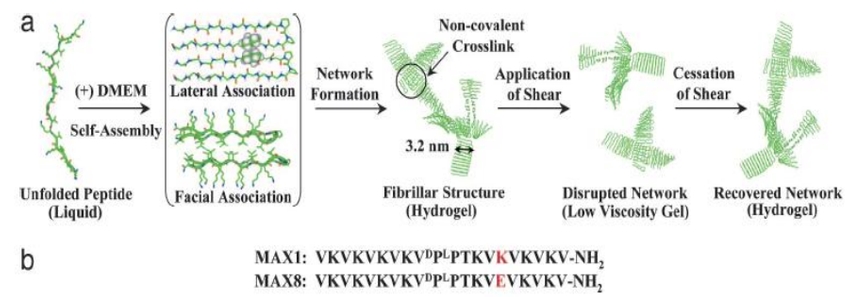
(D) (E)

(A) toroids; (B) Striped cylinders; (c) helix; (D) porous spheres
(E) multicompartment/multigometry micelles.

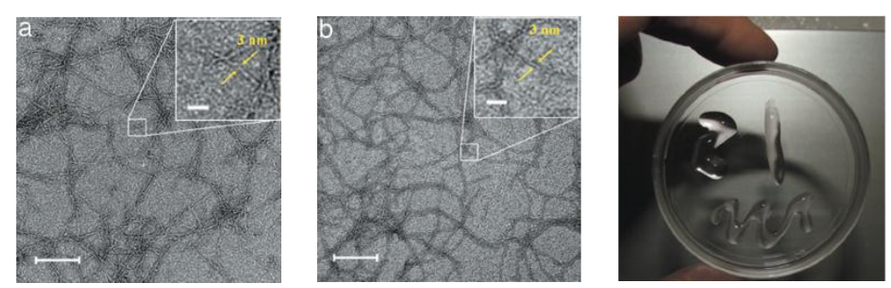
Science. 2004, 306,94
Science. 2007, 317,647
Soft Matter 2008, 4, 90
Nano Letter, 2008,8, 2023
Soft Matter 2011, 7, 2500



Scheme of Max 1 folding and assembly



Scheme of formation of β-hairpin that undergoes a lateral and facial self-assembly affording a rigid hydrogel with a fibrillar supermolecular structure.



(F) (G) (H)

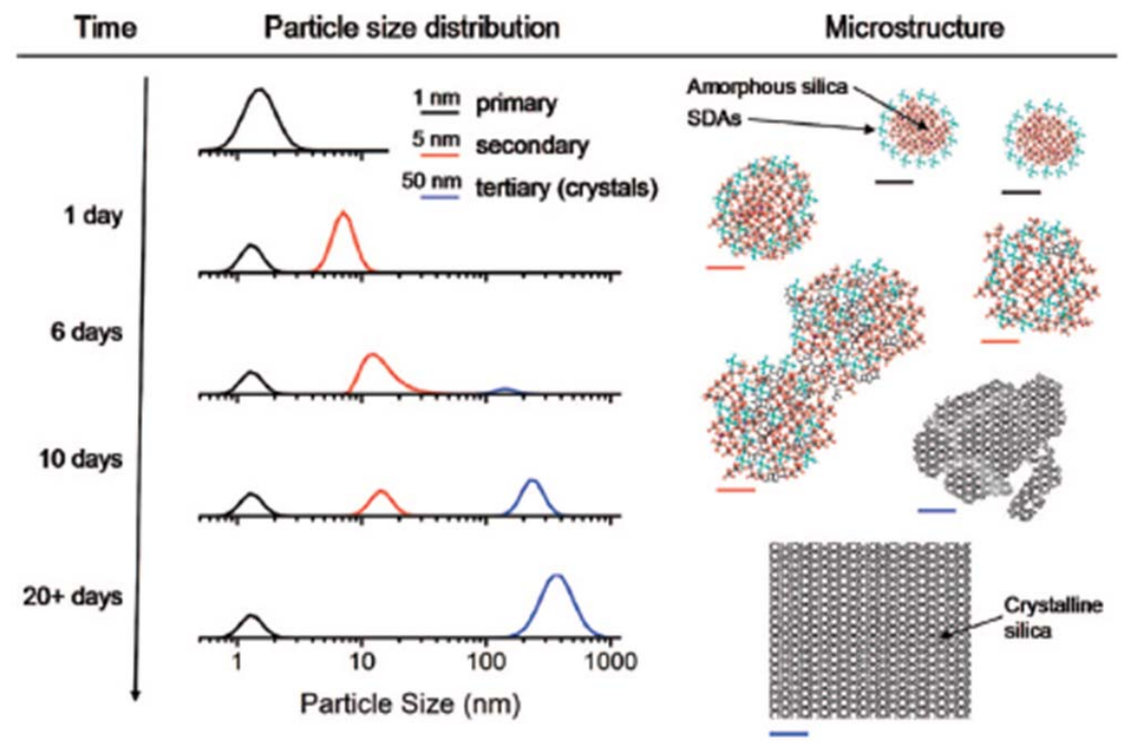
(F): fibril structure formed by MAX1 (G): fibril structure formed by MAX8; (H): MAX8 hydrogels prepared in a syringe

PNAS, 2007, 104, 7791
Biomaterial, 2008, 29, 4164
JACS, 2005, 127, 17025
Soft Matter, 2010, 6, 5143.

The Self-Assembly of Zeolite Catalysts

- *Zeolite beta* is a model material to study the effects of Al and B heteroatom substitutions and structure directing agents (SDA) on zeolite nucleation and growth rates because it can be synthesized with Si to heteroatom ratios from 3 to ∞.

- *SSZ-63* has the same structure with zeolite beta but in a highly ordered fashion and the particles.



The intergrowth of colloid *zeolite beta* and particles size distribution simulated by SAXS & SANS

→ The aim of this project is to understand why the mirco-structure of these two zeolites is so different. X-Ray & Neutron Scattering (SAXS, SANS and USANS) are necessary to characterize the processes of crystal growth and formation.

Center for the Exploration of Energy and Matter

And Department of Physics

RESEARCH at INDIANA UNIVERSITY

Sokol's Research Group

Our research efforts focus on the microscope structure and dynamics of condensed matter using x-ray and neutron scattering techniques.

SANS Science Applications Polymers

Molecular self-assembly and interactions in complex fluids; Colloids and microemulsions; Micelles;

Materials Science

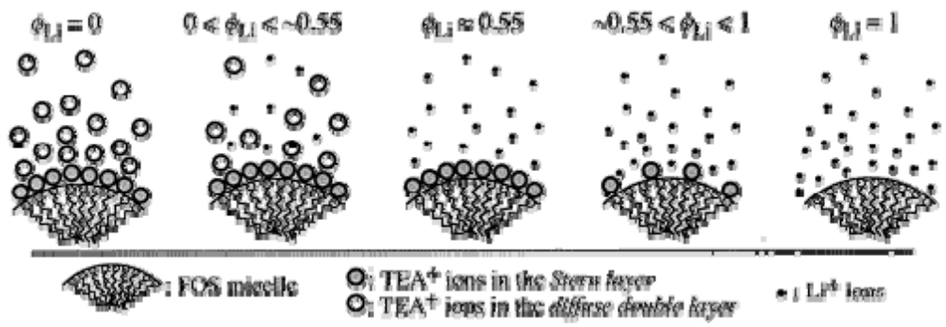
Phase separation in alloys and glasses; Morphologies of superalloys; Nanocomposites

Biological Macromolecules

Size and shape of proteins; macromolecular complexes Hierachical biological structures; Biomembranes

Low Energy Neutron Source

Surfactant Studies



Bossev, et.al., J. Phys. Chem. B 1999, 103, 8259-8266