CHEMICAL ENGINEERING
UNIVERSITY of WASHINGTON

Interfacial Structure of Emulsions

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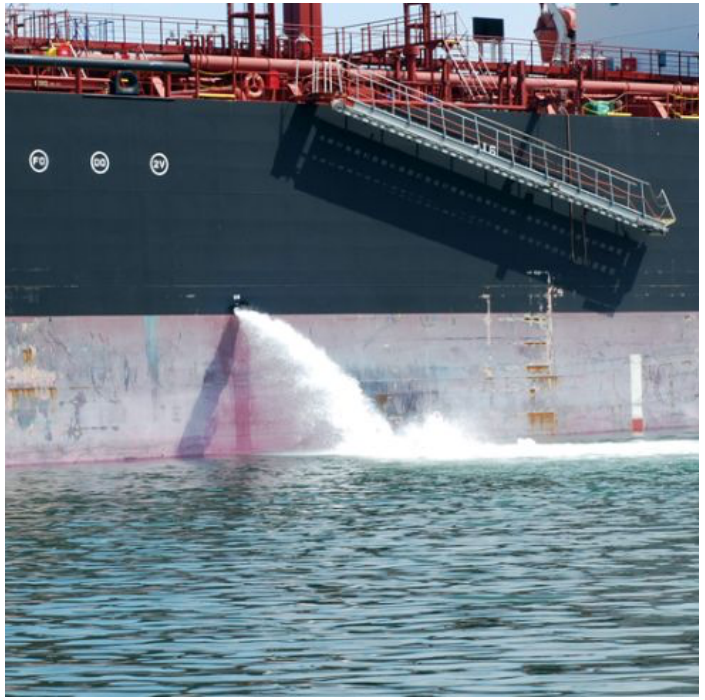
SERDP • ESTCP
25 YEARS OF ESTCP
SYMPOSIUM
2019 | Enhancing DoD's Mission Effectiveness

Managing Fluid-Fluid Interfaces to Enhance DoD Mission Effectiveness

Understanding and Controlling Interfaces of Emulsions and Foams is Critical to DoD Activities

Ballast / Bilge Water Management

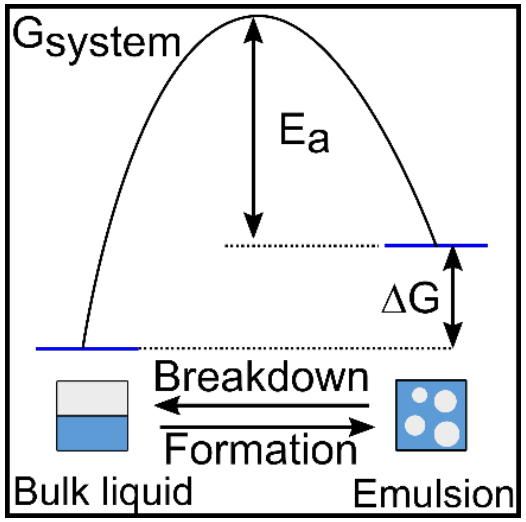


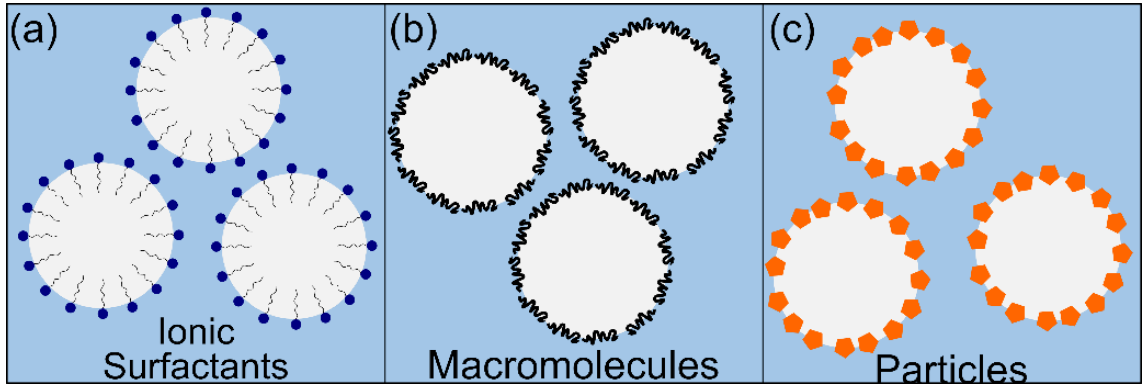
Oil Spills, Fuel De-Watering

Fire Fighting Foams, PFOA/PFOS Cleanup

Emulsion Interfaces and Effects on Stability

- Emulsion Systems are Extremely Diverse
  - Oil-in-Water, Water-in-Oil, Oil-in-Oil
  - Micro-Emulsions, Mini-Emulsions, Nano-Emulsions
  - Particle (Pickering), Polymer and Surfactant Stabilized
- Thermodynamically Unstable (Except Micro-Emulsion)
- Kinetically Stable
  - Stability varies with Structure and Composition (minutes to years)
- Characterizing Interface is Key
- Transport in Emulsions
  - Ostwald Ripening
  - Coalescence Rates

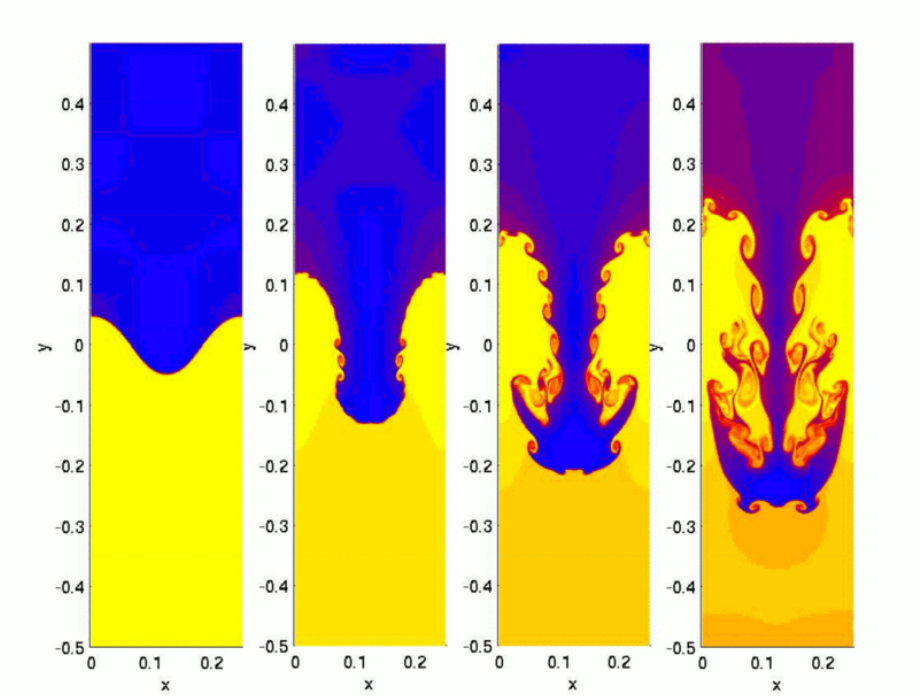




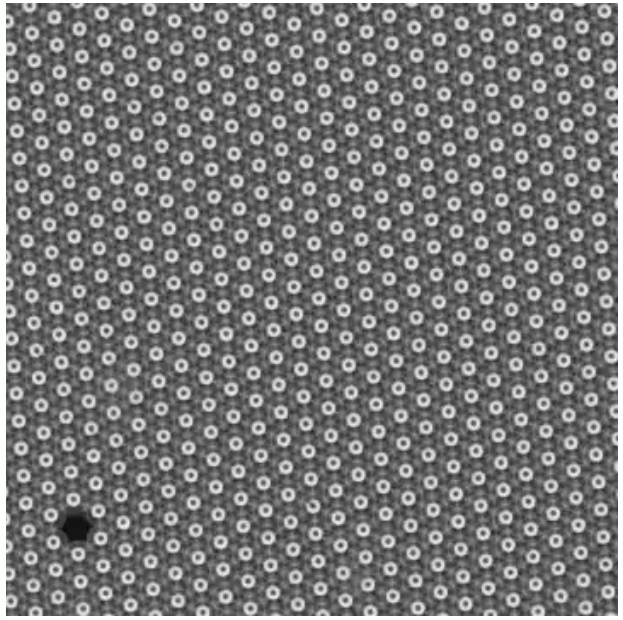
Breaking and Making Emulsion Interfaces

- Making Emulsions
  - Mechanical (Shear, Turbulence, Cavitation / Ultrasound)
  - Spontaneous Emulsification (Solubilization, the Ouzo Effect)

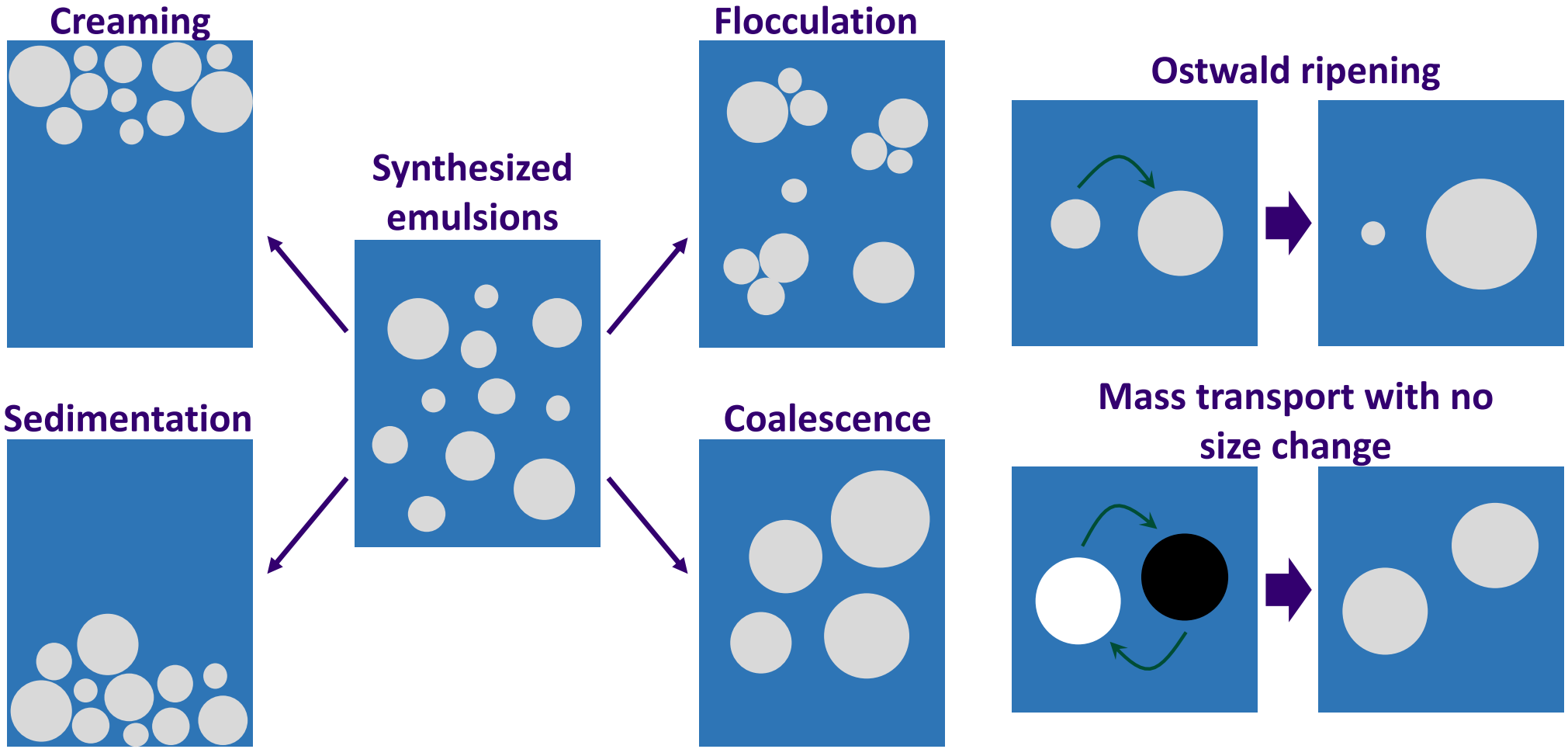
- Breaking Emulsions
  - Ostwald Ripening
  - Mechanical Methods
  - Electro-hydro-dynamic
  - Centrifugation
  - Flocculation
  - Chemical Demulsification



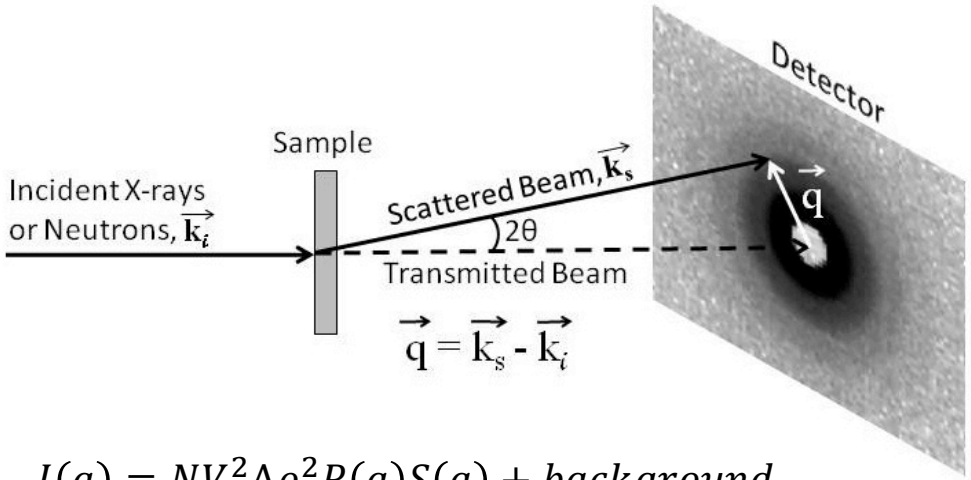
Taccoen and Baroud (PRL)



On the 'Life and Death' of an Emulsion System



Small Angle Neutron and X-ray Scattering Basics



$$I(q) = NV_p^2 \Delta\rho^2 P(q) S(q) + background$$

P(q): single particle (form factor)

S(q): inter-particle (structure factor)

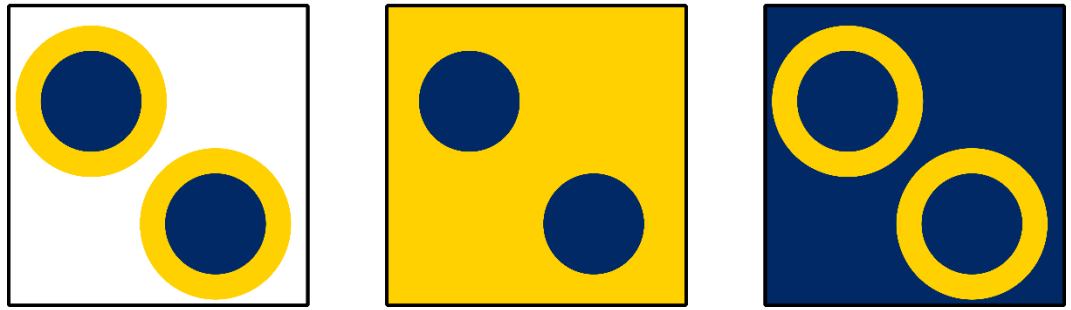
$$\Delta\rho^2 = (SLD_{emulsion} - SLD_{solvent})^2$$

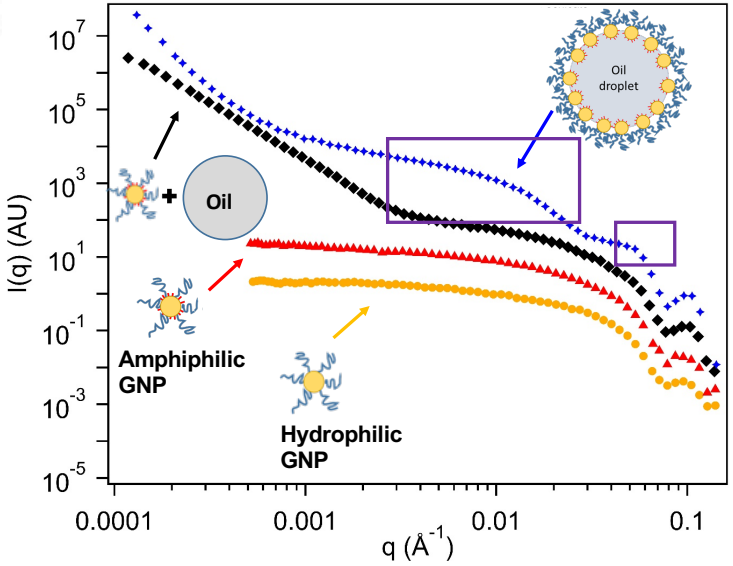
SLD: scattering length density

Hexadecane: SLD = -0.426 *10^{-6} Å^{-2}

D-Hexadecane: SLD = +6.664*10^{-6} Å^{-2}

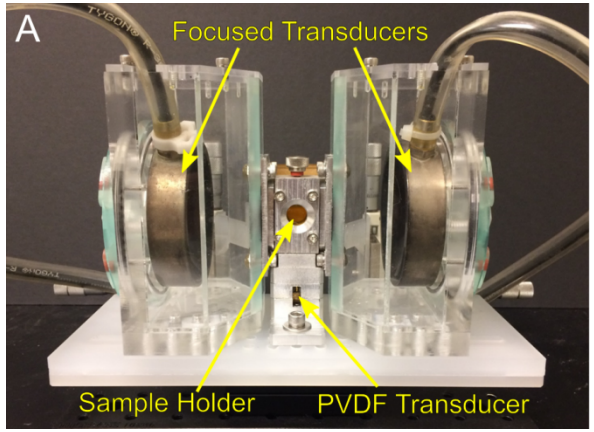
Contrast Variation Small Angle Neutron Scattering (CV-SANS)





Large Size Scale (µm) Small Size Scale (nm)

In-Situ Ultrasound Analysis



Small Angle Scattering Model for Pickering Emulsions

$$I_{Total}^{Mono}(q) = I_{op}^{Mono}(q) + I_{p}^{Mono}(q)$$

$$I_{op}^{Mono}(q) = \left(\varphi_o(\Delta\rho_o)^2 V_o + \varphi_p^T \varphi_p^a N_p (\Delta\rho_p)^2 V_p\right) P_{op}$$

$$I_{p}^{Mono}(q) = \varphi_p^T (1-\varphi_p^a)(\Delta\rho_p)^2 V_p \psi_p^2$$

$$\psi_p = \frac{3[\sin(qR_p) - qR\cos(qR_p)]}{(qR_p)^3}$$

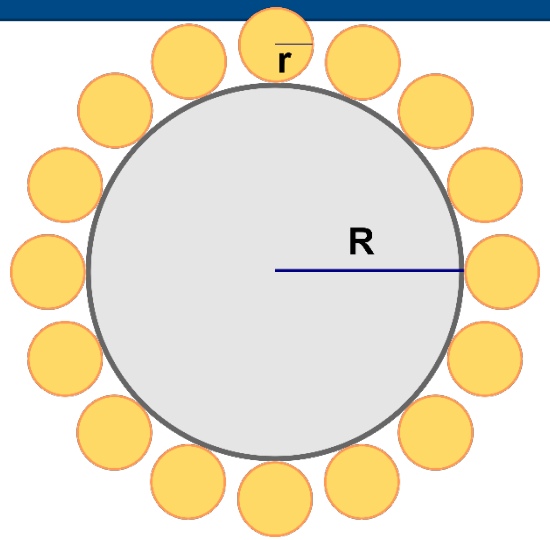
$$\psi_o = \frac{3[\sin(qR_o) - qR\cos(qR_o)]}{(qR_o)^3}$$

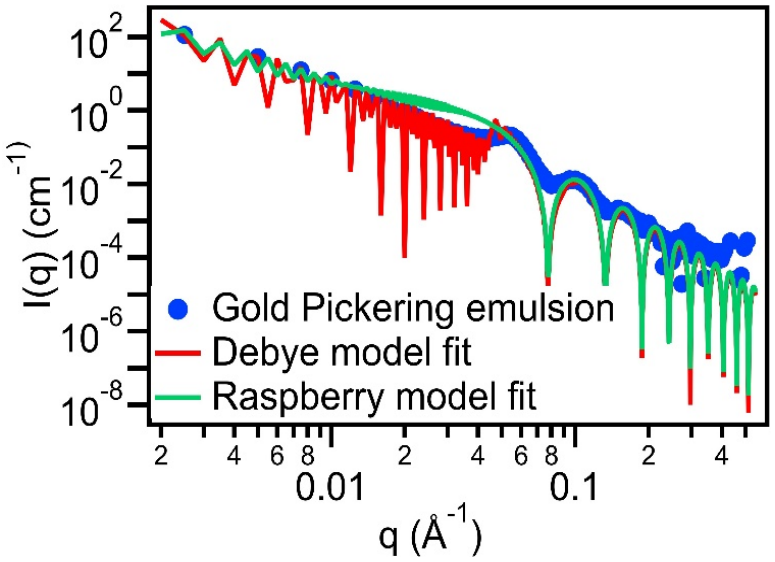
$$P_{op} = \frac{1}{M^2}\left[\begin{array}{c}(\Delta\rho_o)^2 V_o^2 \psi_o^2 + N_p(\Delta\rho_p)^2 V_p^2 \psi_p^2 \\ +N_p(N_p-1)(\Delta\rho_p)^2 V_p^2 S_{pp} + 2N_p \Delta\rho_o \Delta\rho_p V_o V_p S_{op}\end{array}\right]$$

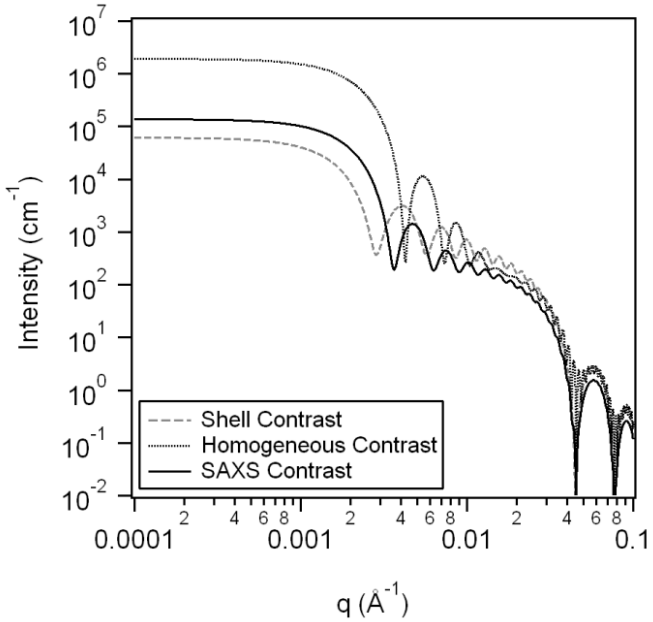
$$M = \Delta\rho_o V_o + N_p \Delta\rho_p V_p$$

$$S_{op} = \psi_o \psi_p \frac{\sin(q(R_o+\delta R_p))}{q(R_o+\delta R_p)}$$

$$S_{pp} = \psi_p^2 \left[\frac{\sin(q(R_o+\delta R_p))}{q(R_o+\delta R_p)}\right]^2$$

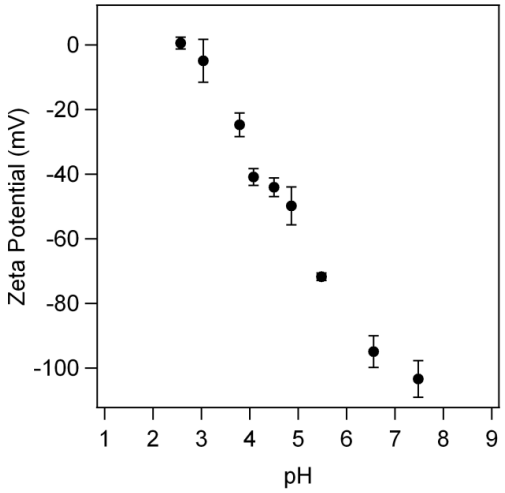


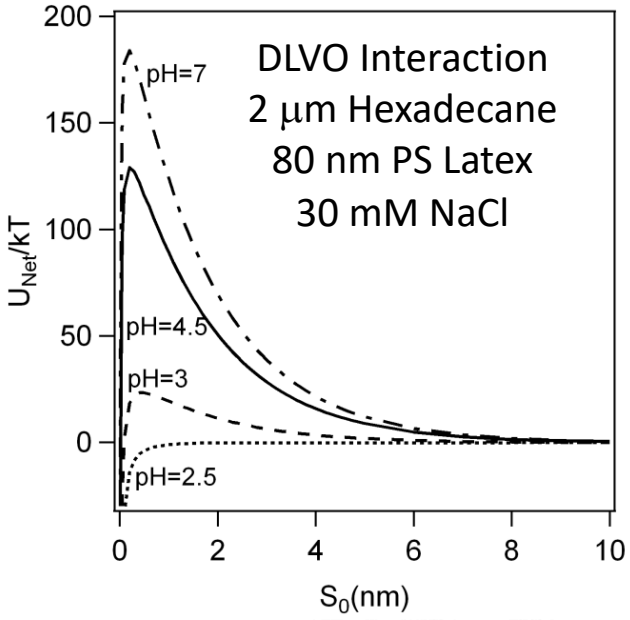


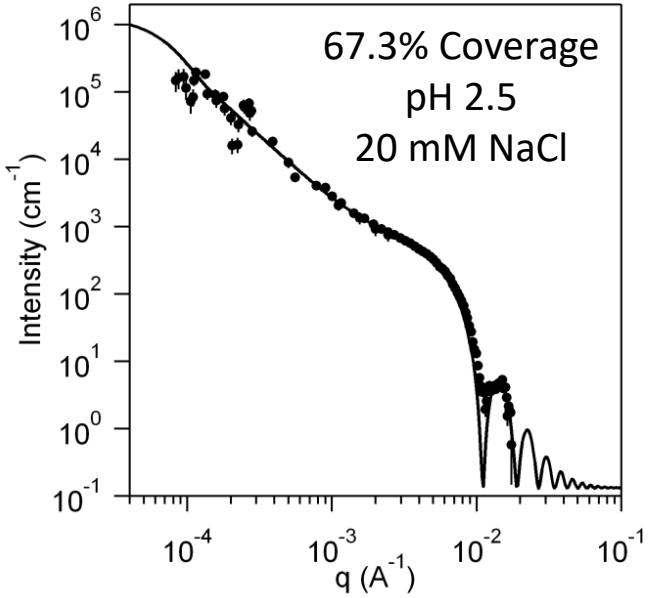


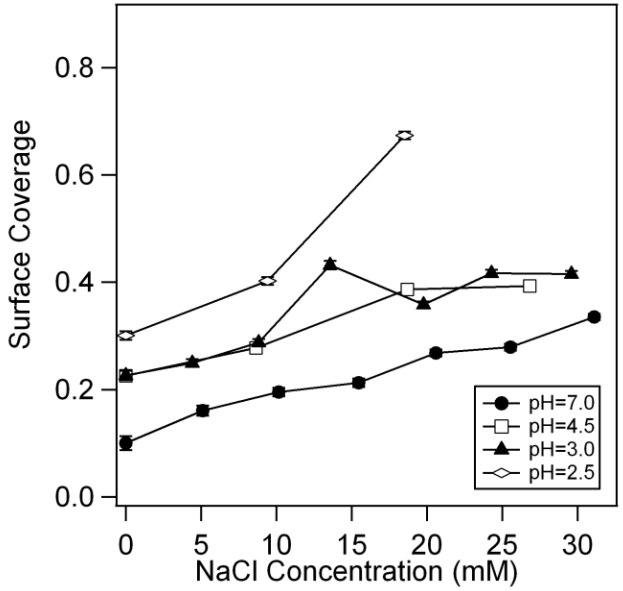
"Small Angle Scattering Model for Pickering Emulsions and Raspberry Particles" Larson-Smith, Jackson and Pozzo, J. Colloid and Interface Science, 343: 36 (2010)

Electrostatic Barriers for Particle Adsorption on Emulsion Interfaces

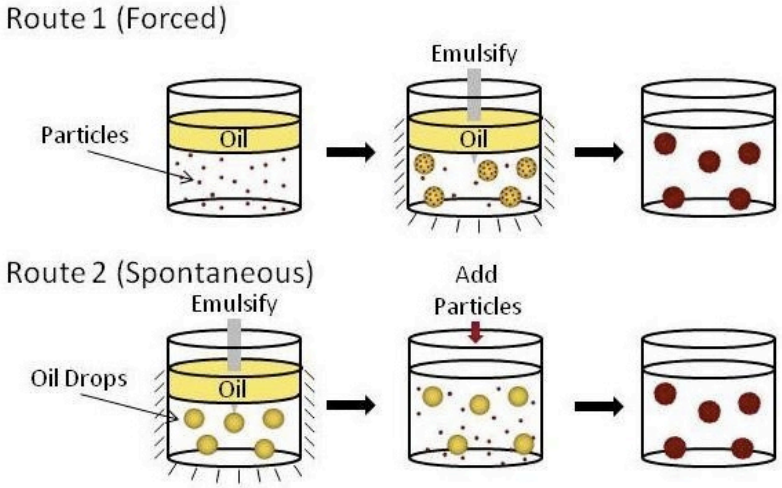






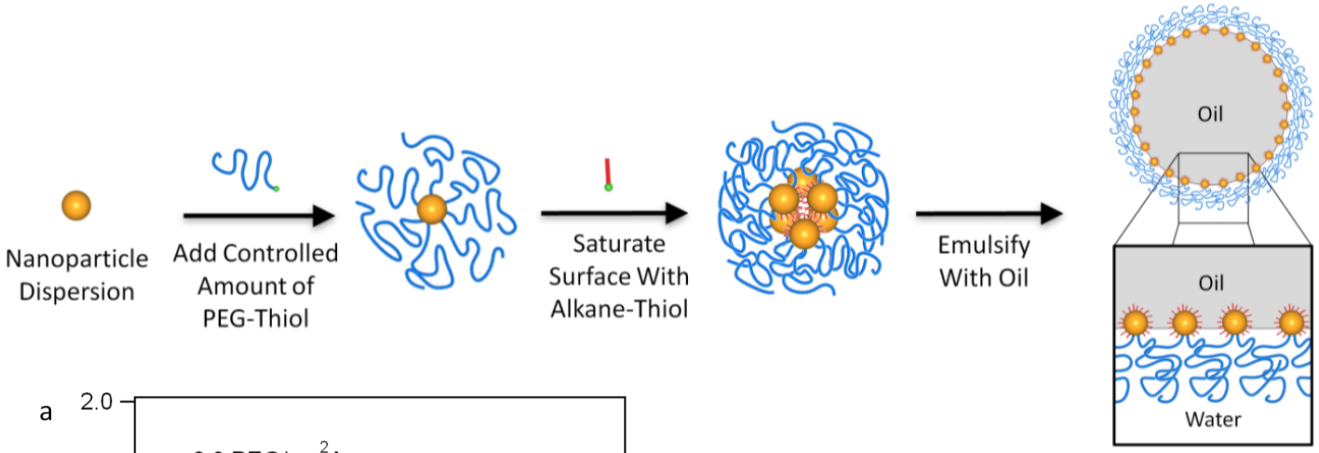


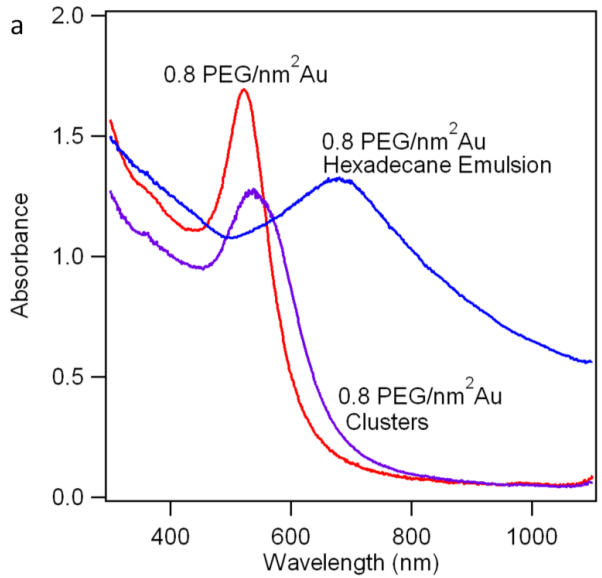
'Bare' Hexadecane Emulsions are Negatively Charged due to OH^- ion adsorption

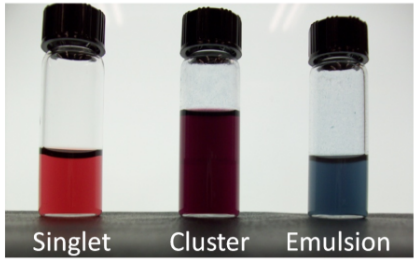


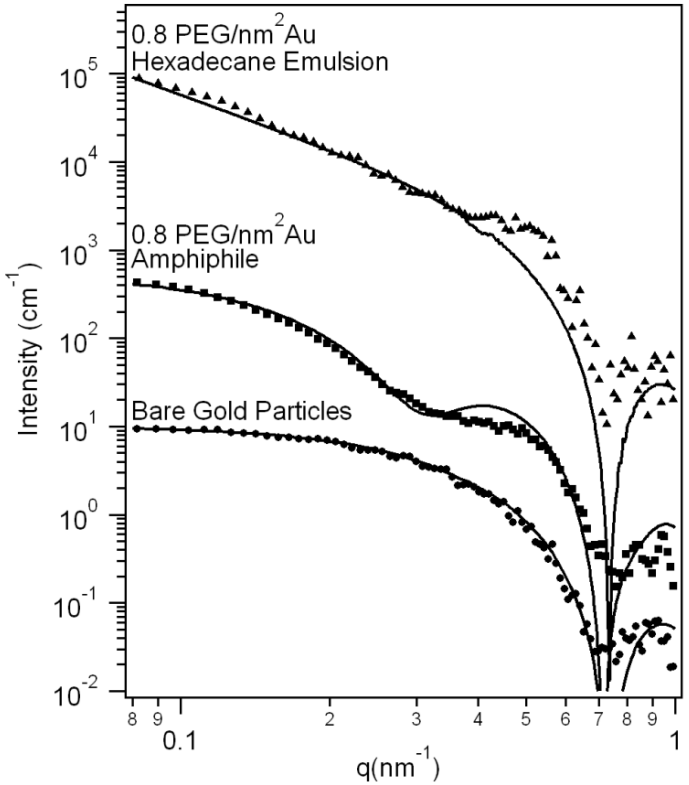
"SANS and SAXS Analysis of Charged Nanoparticle Adsorption at Oil-Water Interfaces" Larson-Smith, Jackson and Pozzo, Langmuir, 28: 2493 (2012)

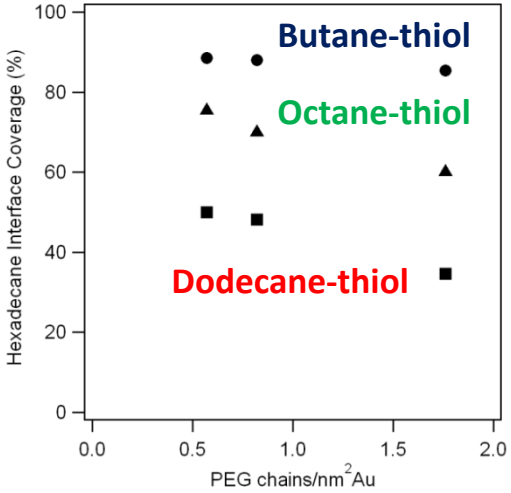
Emulsions Stabilized by Nanoparticle Surfactants





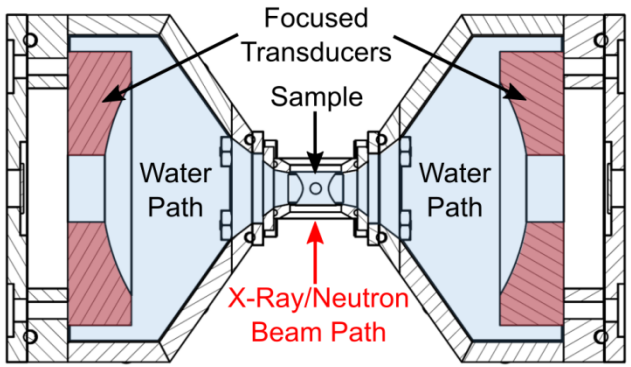


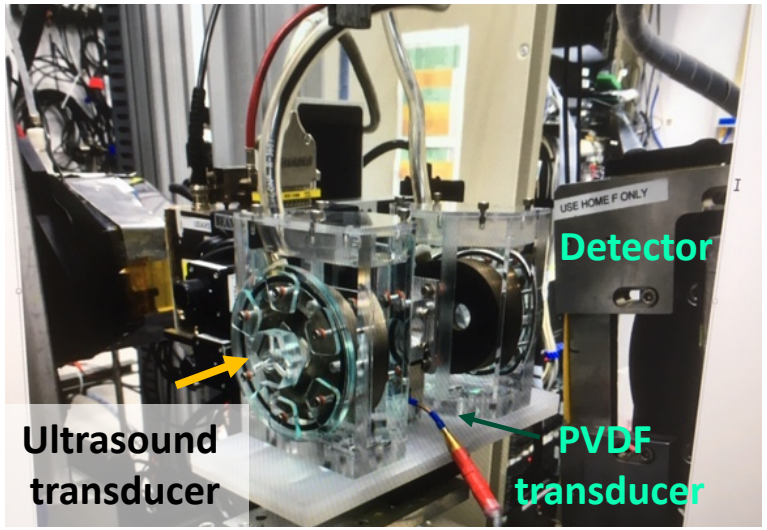


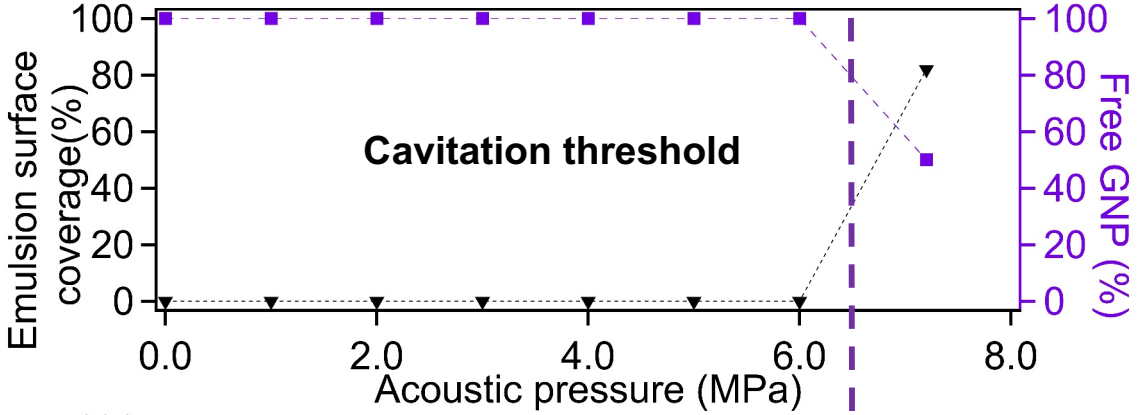


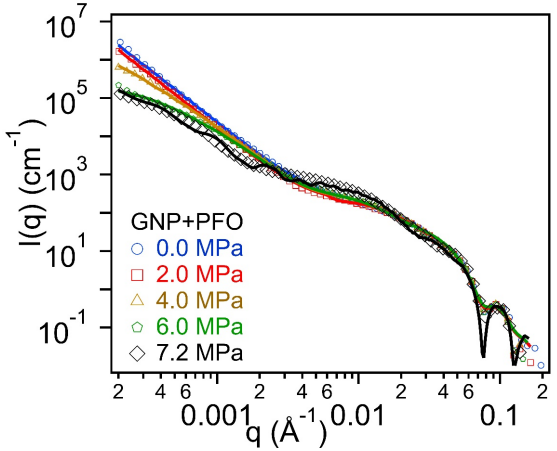
"Pickering Emulsions Stabilized by Nanoparticle Surfactants"
Larson-Smith, Pozzo, Langmuir, 28(32): 11725 (2012)

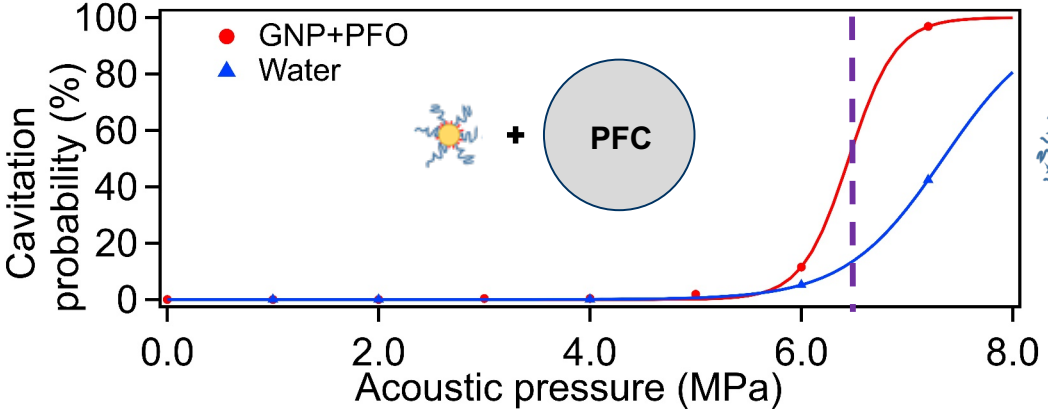
Ultrasound Formation of Particle Stabilized Emulsions

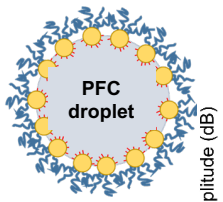


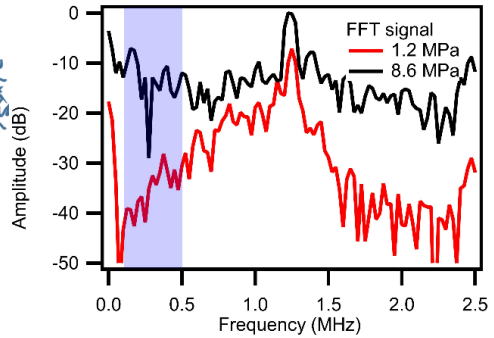










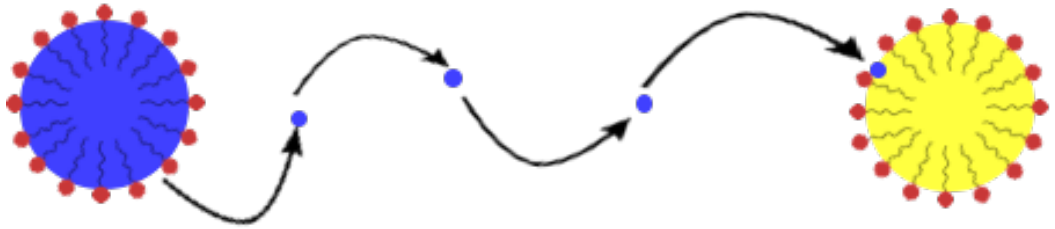


"Ultrasound-based formation of nano-Pickering emulsions investigated via in-situ SAXS" Lee, Li, Ilavsky, Kuzmenko, Jeng, O'Donnell, Pozzo, Journal of Colloid and Interface Science, 15, 281. (2019)

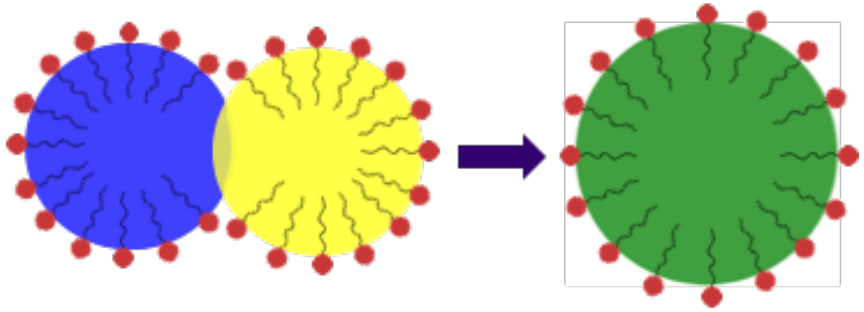
Mass Transport in Emulsion Systems

Surfactant stabilized emulsions

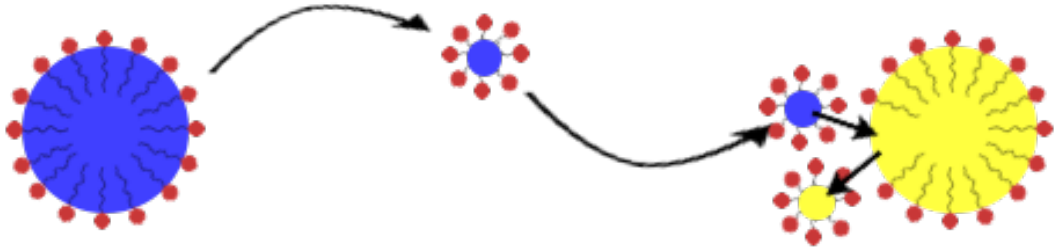
Oil diffusion through aqueous phase



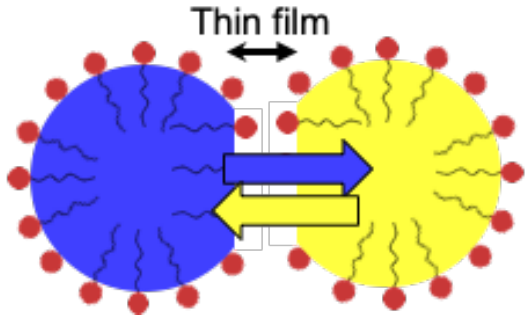
Coalescence



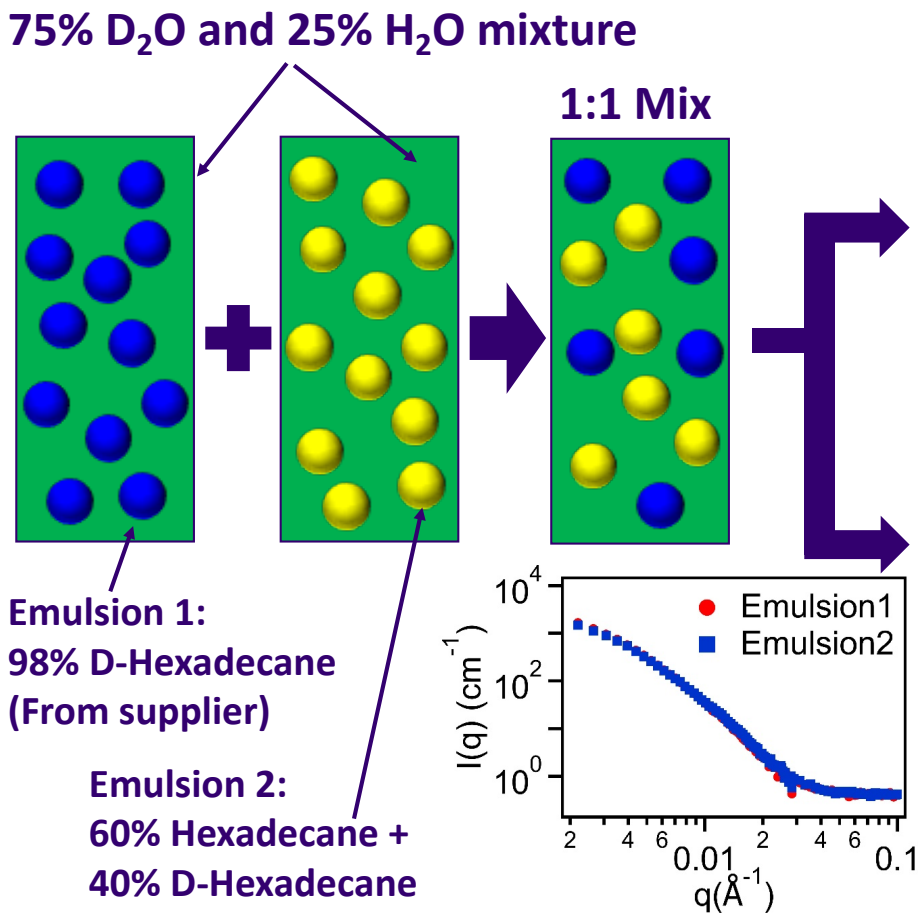
Micelle carrying oil molecules (swollen micelles)

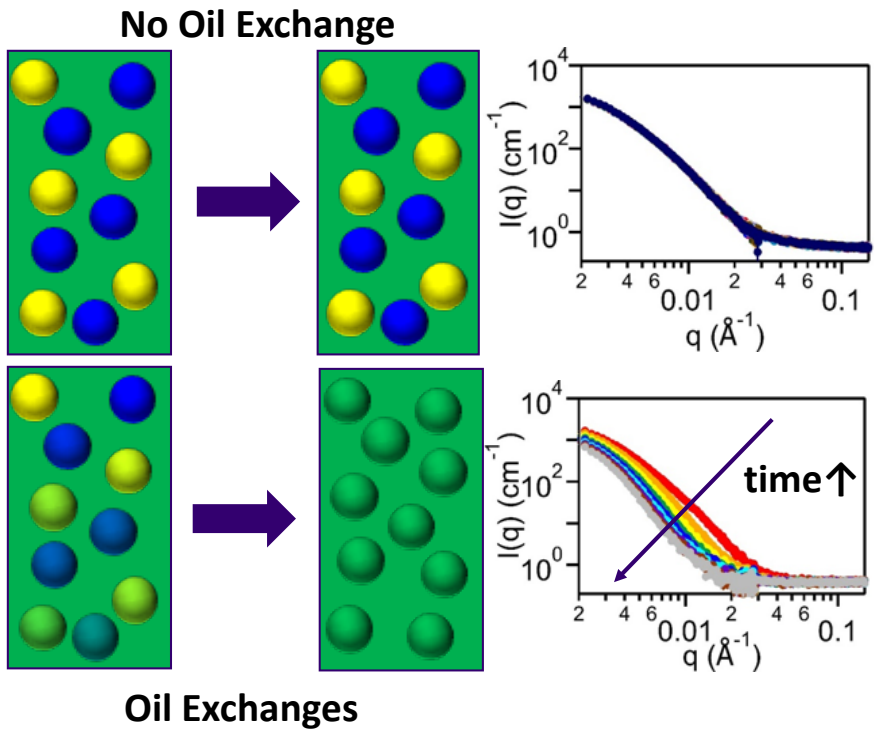


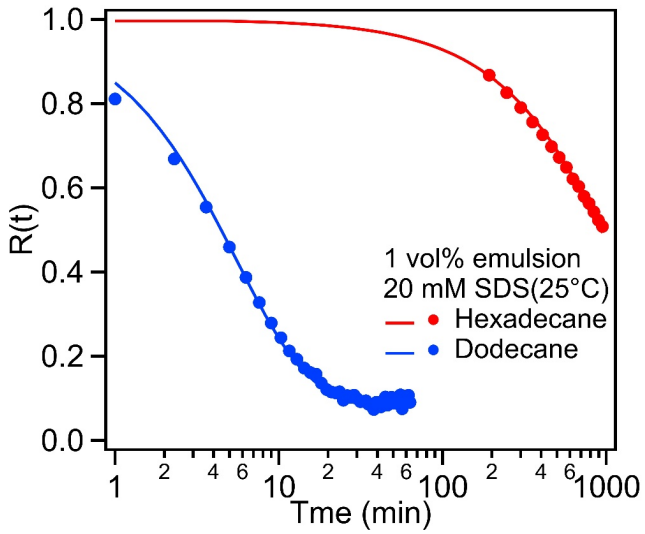
Formation of flocs



CV-SANS Analysis of Mass Transport in Emulsion Systems





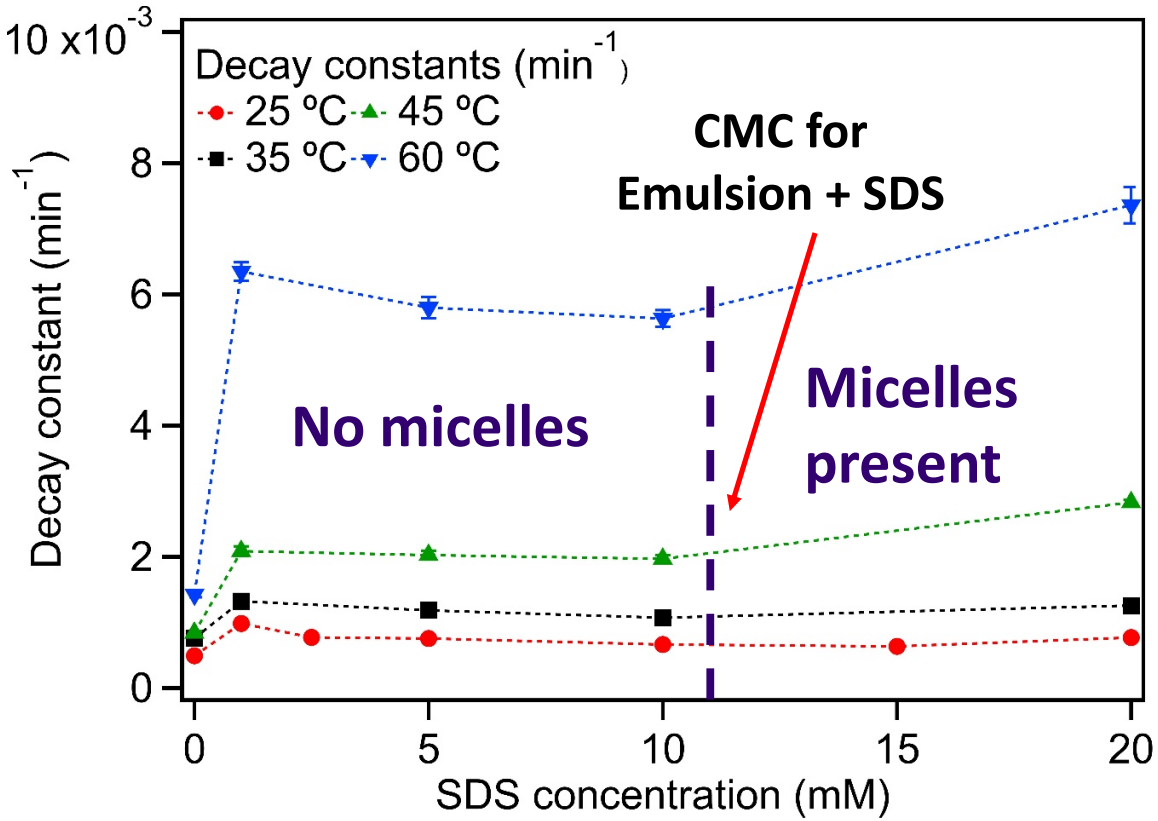


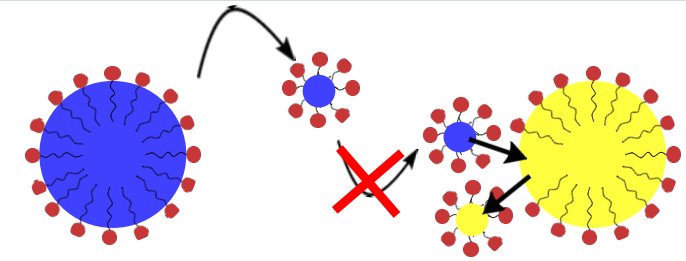
$$I(q) = NV_p^2 \Delta\rho^2 P(q)S(q) + background$$

$$R(t) = \left(\frac{I(t) - I_\infty}{I_0 - I_\infty}\right)^{1/2} \propto \Delta\rho$$

"Contrast-variation Time-resolved SANS Analysis of Oil Exchange Kinetics Between Oil-in-water Emulsions Stabilized by Anionic Surfactants" Lee and Pozzo, Langmuir, DOI: 10.1021/acs.langmuir.9b02423

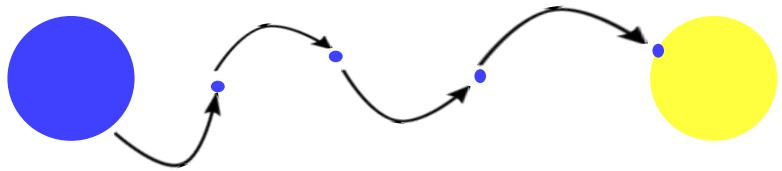
CV-SANS Analysis of Mass Transport in Emulsion Systems





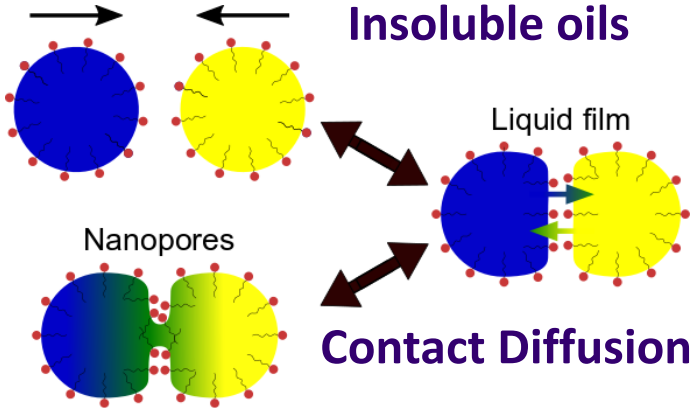
Micelle Driven Transport Negligible

More soluble oil



Molecular Diffusion

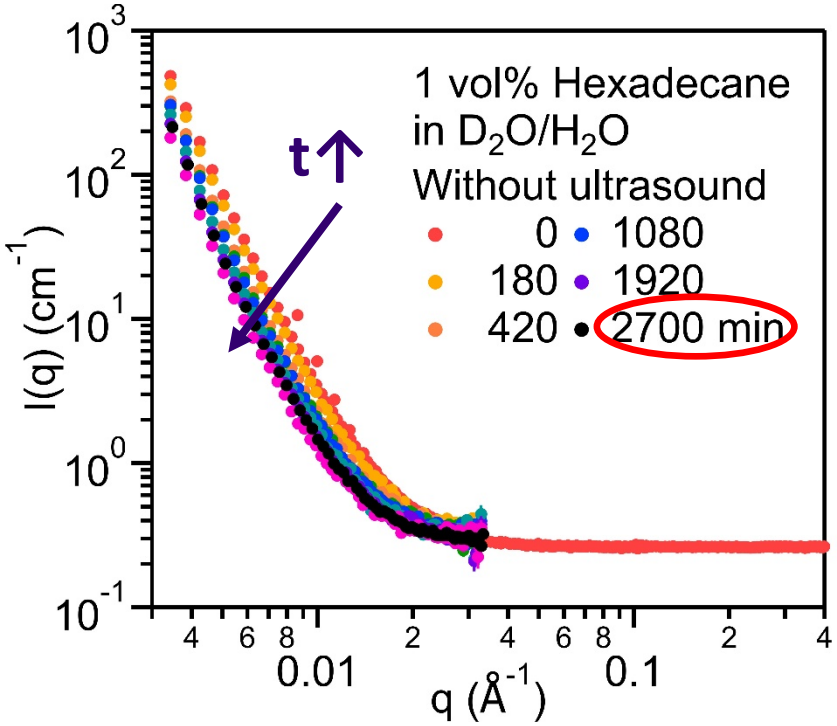
Insoluble oils



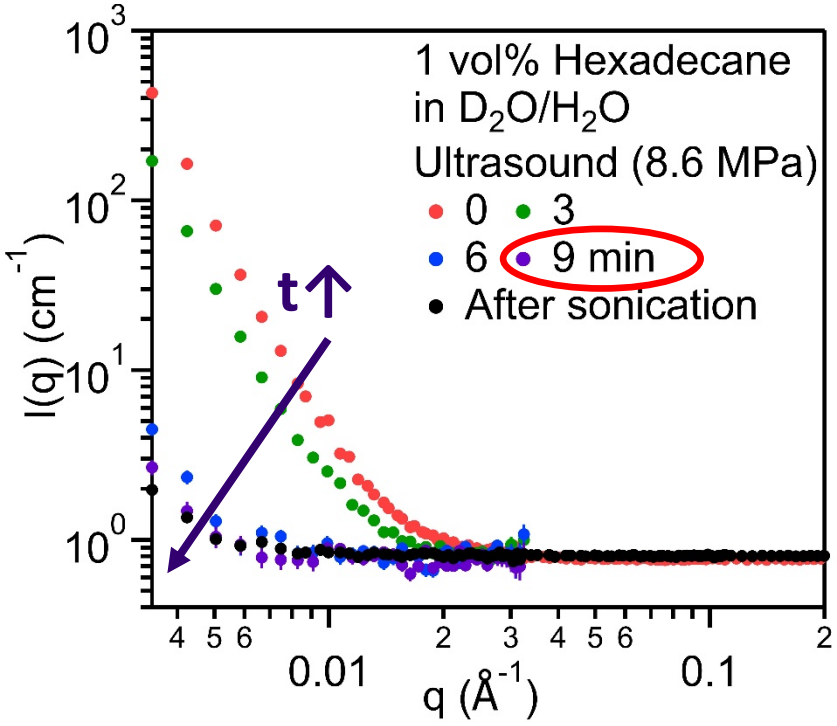
Contact Diffusion

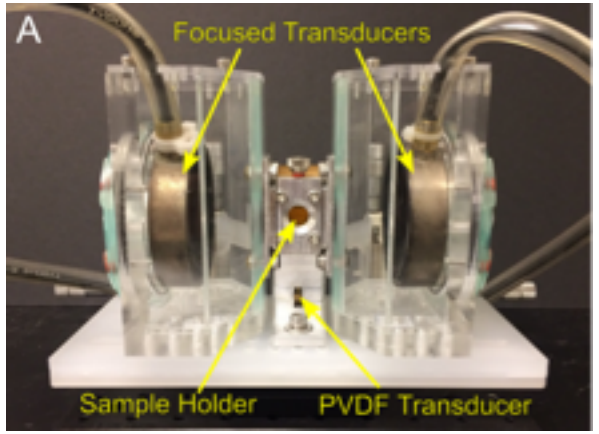
Ultrasound Induced Mass Transfer in Emulsion Systems

Emulsions at rest and no surfactants present



Sonicated at high acoustic pressures

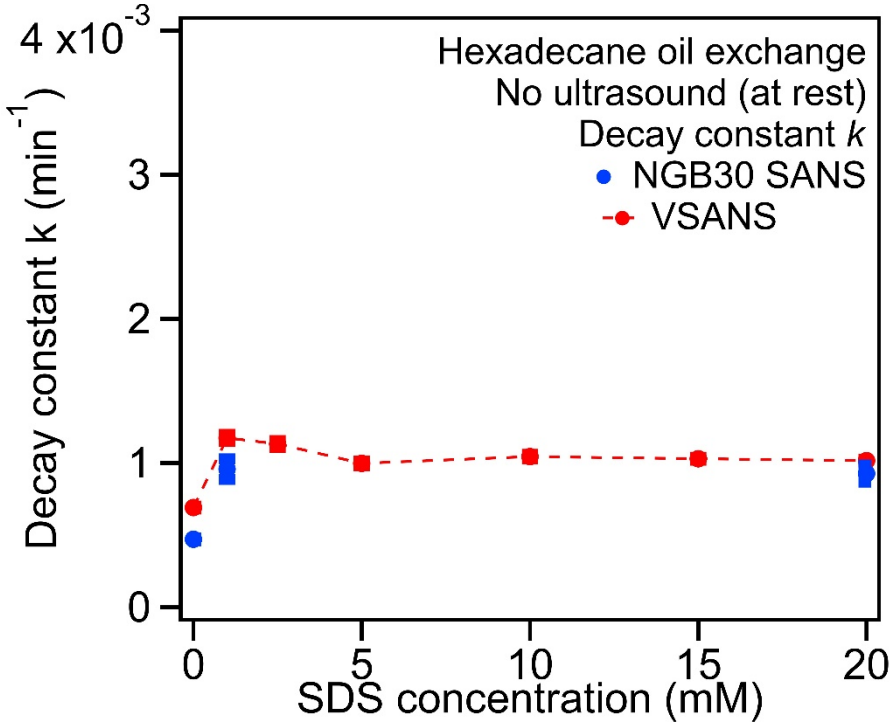




"Kinetic Analysis of Ultrasound Induced Oil Exchange in Oil-in-water Emulsions through Contrast Variation Time-resolved SANS" Lee, Li and Pozzo, Langmuir, DOI: 10.1021/acs.langmuir.9b02424

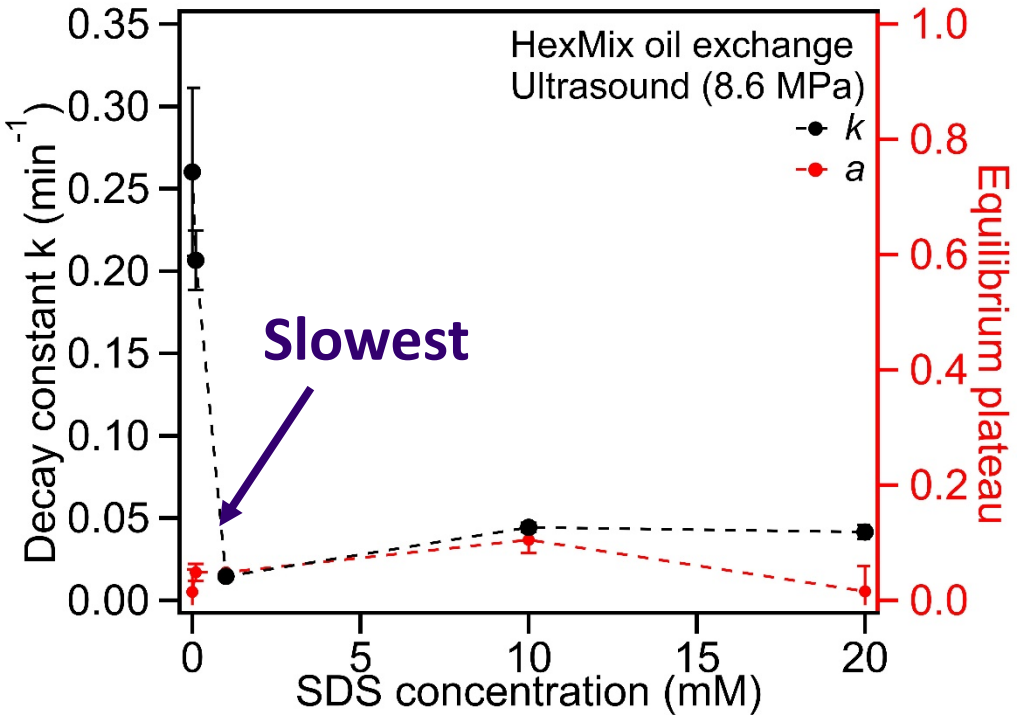
Effect of Surfactant Concentration on Oil Exchange Rest vs. Ultrasound

Spontaneous exchange



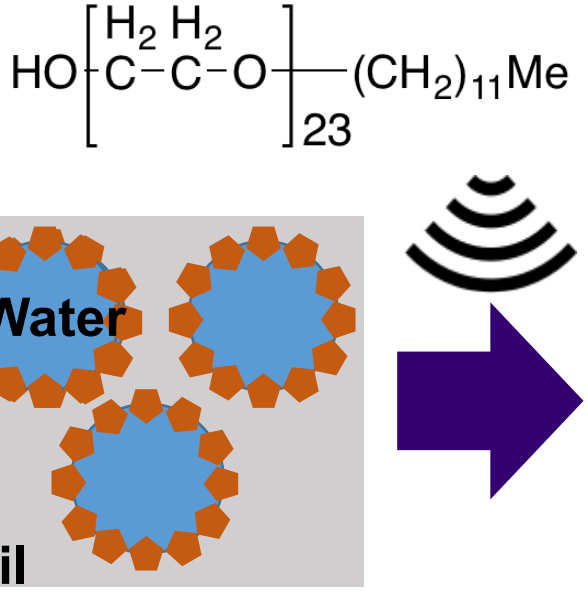
Opposite trend

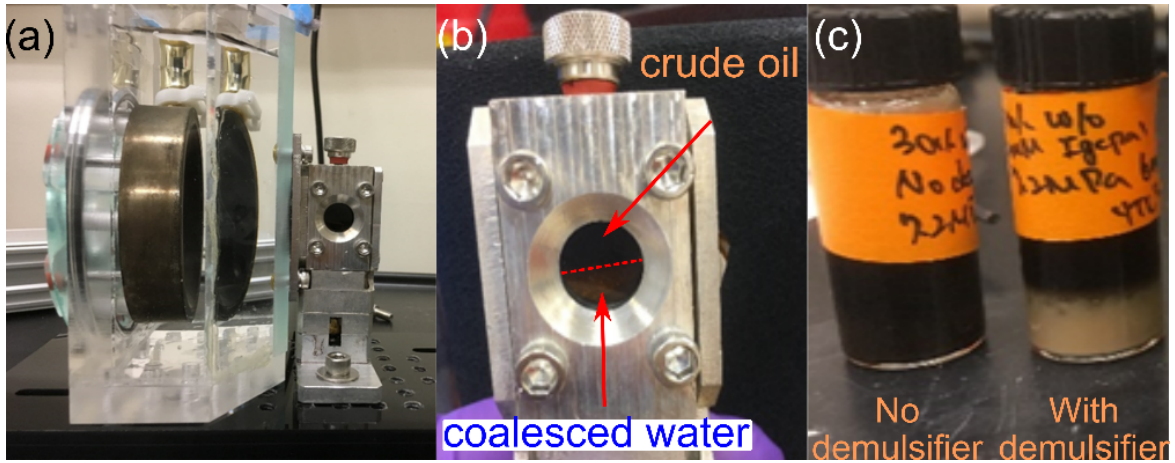
Ultrasound induced exchange

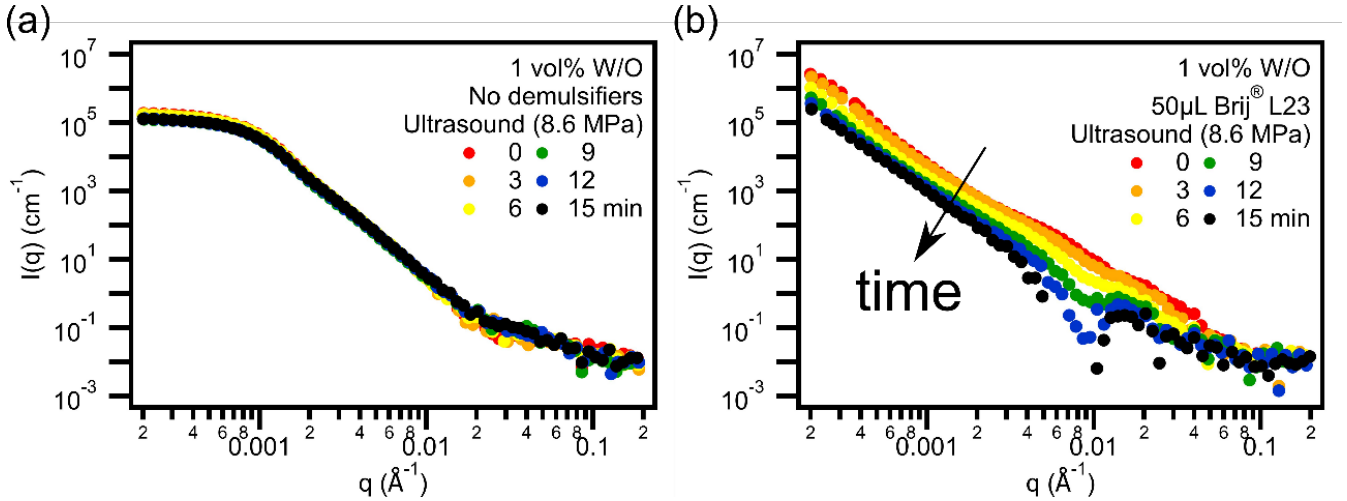


Ultrasonic-Assisted Demulsification of Water-in-Oil Emulsions

- Particle stabilized water-in-oil emulsions are commonly formed in the oil industry
  - Add demulsifiers (hydrophilic polymer, e.g. Brij® L23) to replace particles
  - Additional treatment: e.g. apply ultrasound







Conclusions

- Small Angle X-ray and Neutron Scattering are Invaluable Tools for the Study of Emulsion Interfaces
- Need to Understand how Colloidal Interactions Change as Interfaces are Modified
- In-situ Evaluation of Emulsions Under External Fields is Possible
  - Ultrasound, Electric, Magnetic, any…
- CV-SANS Allows Analysis of Mass Transport of Molecules Across Emulsion Interfaces
- Opportunities of Analyze Realistic Emulsion Systems
  - Emulsification / Demulsification of Crude Oil or Ballast Water

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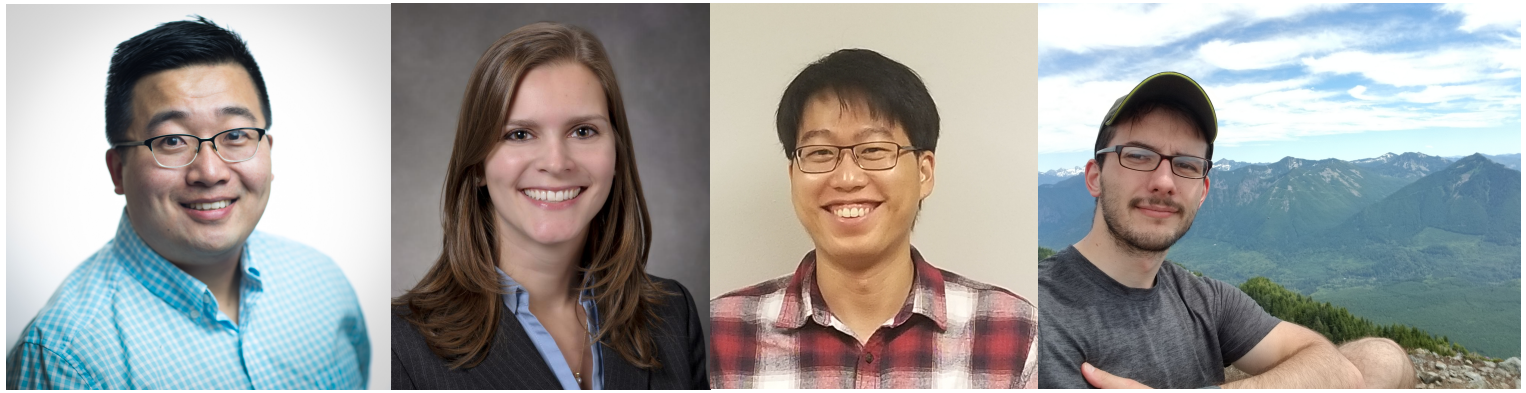

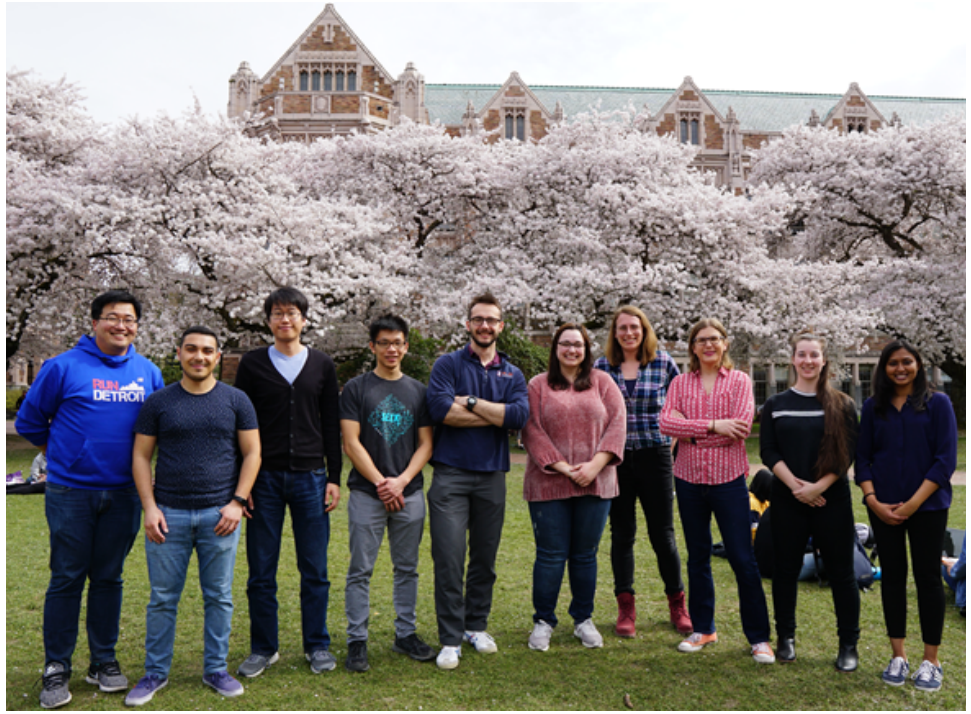

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