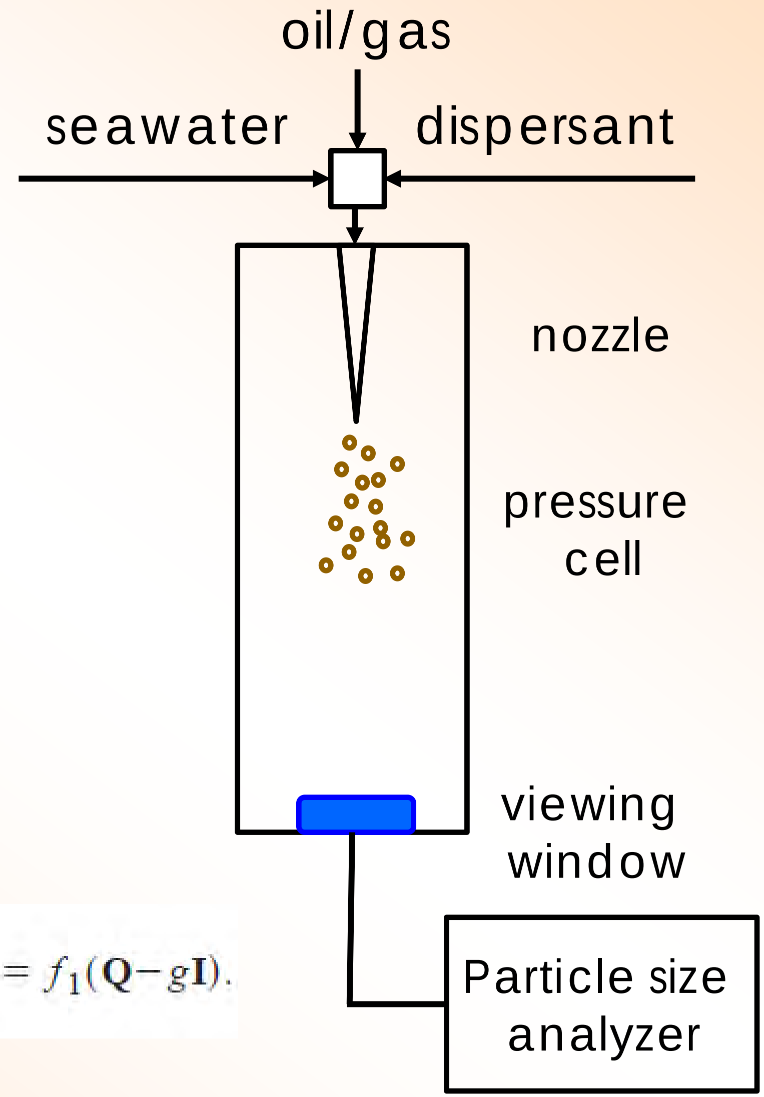
Drop Size Distribution in Emulsification of Seawater, Oil and Dispersants

- Test bed under construction to measure drop size and size distribution of sea water, oil and dispersants in high speed jets
- Two and three phase jet flow
- Dispersant evaluation tool
- Droplet break-up models
  - Evolution of Q shape factor to break-up
  - Modified Maffettone & Greco model for high shear

$$\frac{d\mathbf{Q}}{dt} - (\boldsymbol{\Omega}\cdot\mathbf{Q} - \mathbf{Q}\cdot\boldsymbol{\Omega}) + a(\mathbf{D}\cdot\mathbf{Q} + \mathbf{Q}\cdot\mathbf{D}) + b\mathbf{D}:\mathbf{Q}\mathbf{I} + c\mathbf{D}tr(\mathbf{Q}) = f_1(\mathbf{Q} - g\mathbf{I}).$$

Maffettone & Greco *JOR* 2004



Computational Studies of Hydrate Formation and Stability

Pablo G. Debenedetti

Department of Chemical and Biological Engineering, Princeton University

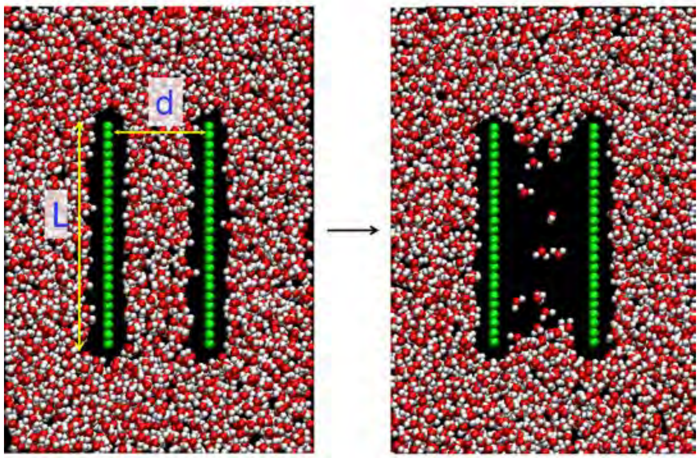
Consortium for Molecular Engineering of Dispersant Systems
Gulf of Mexico Research Initiative

Objectives

- Accurate, molecular-based calculation of rates of methane hydrate formation and dissociation
- Molecular-level insight into mechanisms of nucleation and dissociation across broad ranges of T, P, salinity, supersaturation
- Influence of dispersants on hydrate formation and stability

✓Nucleation ➔ Rare, fast, activated

✓Path-sampling techniques ➔ Forward Flux Sampling (FFS)(*)



Sharma and Debenedetti, *PNAS, 109*, 4365 (2012)

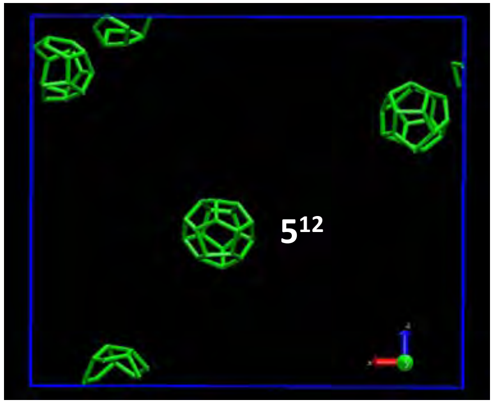
✓Use FFS to compute rates, free energy barriers, identify mechanisms

✓Effects of T, P, salinity, interfaces, dispersants

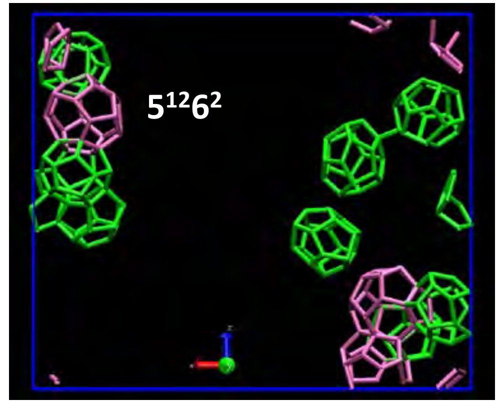
(*) Allen et al., *Phys. Rev. Lett., 94*, 018104 (2005)

μs MD Simulation of Methane Hydrate Homogeneous Nucleation

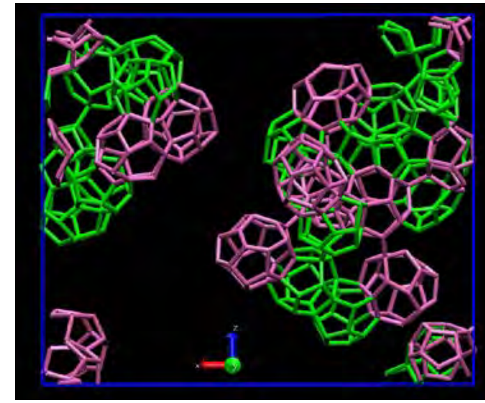
TIP4P/Ice & united atom LJ, 220K & 200bar



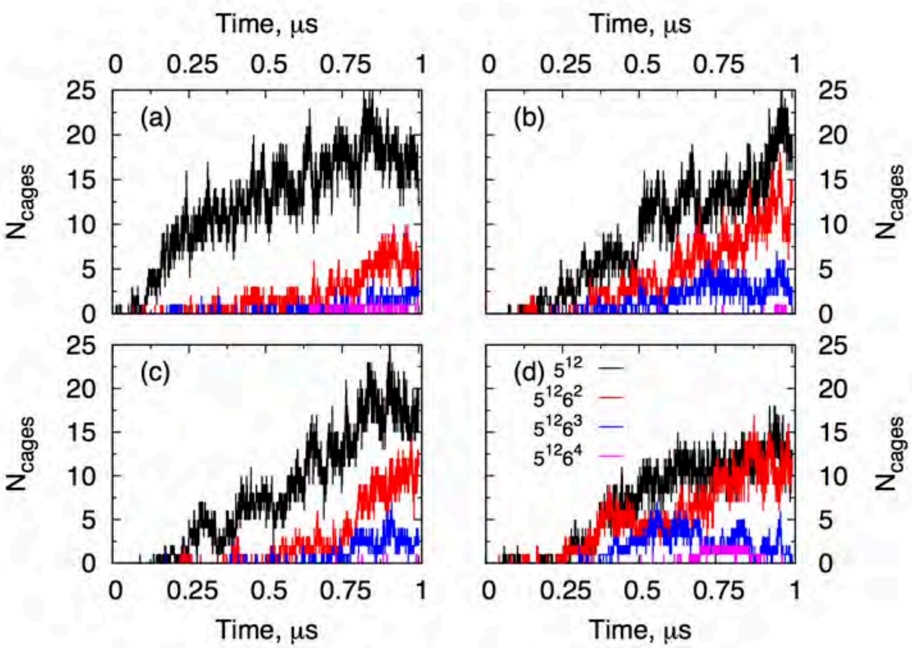
300 ns

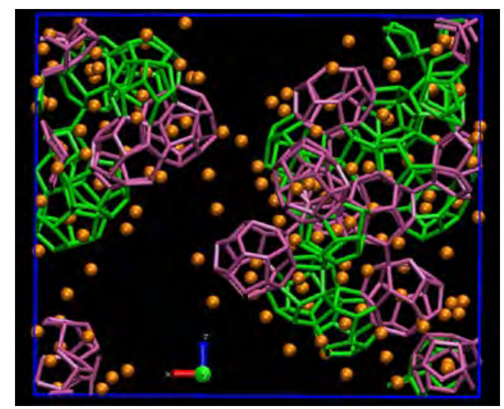


500 ns



1000 ns





1000 ns

PLANS

Implement Forward Flux Sampling for hydrate nucleation

Rate calculations for methane hydrate across broad ranges of (T, P, salinity, supersaturation)

Homogeneous and heterogeneous nucleation (interfaces)

Perform simulations in the presence of propylene glycol & selected surfactants

IMPLICATIONS

Hydrates directly relevant to oil spill prevention and remediation

In Deepwater Horizon disaster, played major role in cofferdam strategy failure

Possible role in original blowout

Immense natural gas resource: 21 TCF of in-place hydrates in Gulf of Mexico

Copolymer-based Dispersants for Oil-drop Stabilization: A Computer Simulation Study

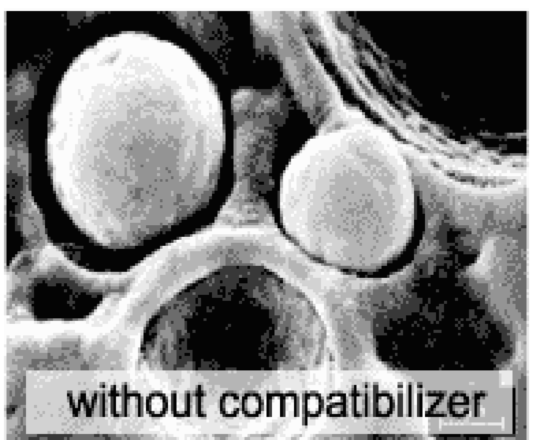
Carol Hall, N. C. State University

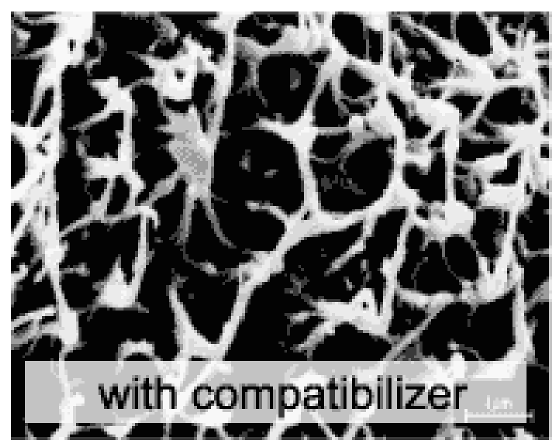
Objective: to discover, through molecular-based simulation, how the sequence of a copolymer-based dispersant impacts the interfacial properties and stability of an oil drop in water.

Analogy

Copolymer Compatibilizers

- Homopolymer blends are immiscible & phase separate
- Copolymer compatibilizers promote miscibility
- AB copolymer– A likes one homopolymer , B likes the other
- :



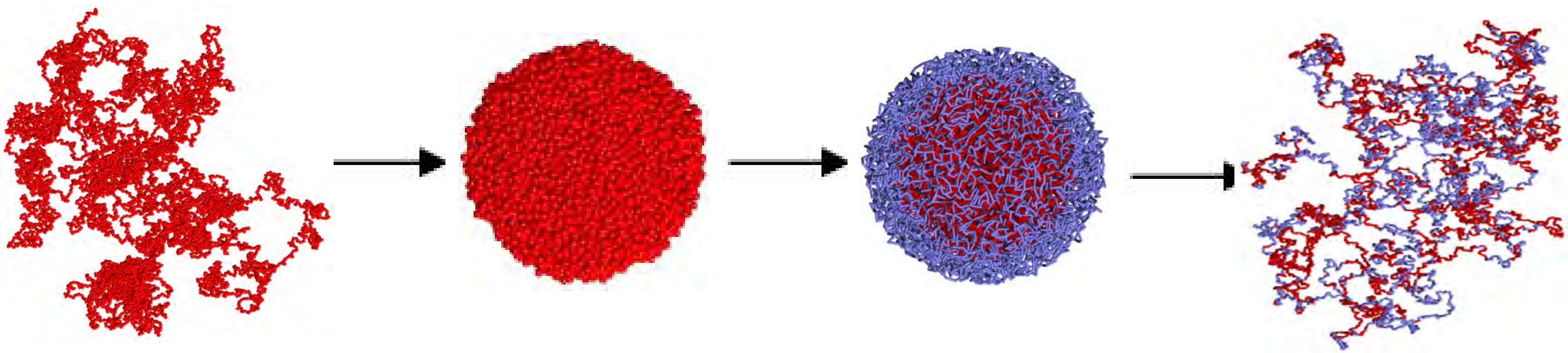


Surfactant –based Dispersants

- Oil and water are immiscible and phase separate
- Surfactants promote miscibility
- Surfactant- head likes water tail likes oil

Protein-like Copolymers

Protein-Like copolymers can be made in the laboratory



Styrene Homopolymer in Coil State

Styrene Homopolymer (C) Globule State

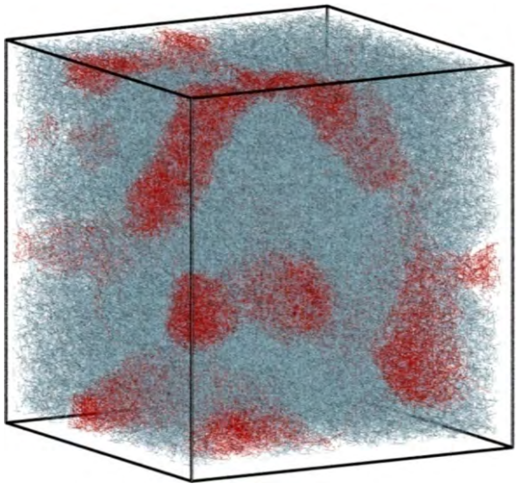
Outer styrene segments reacted with bromine

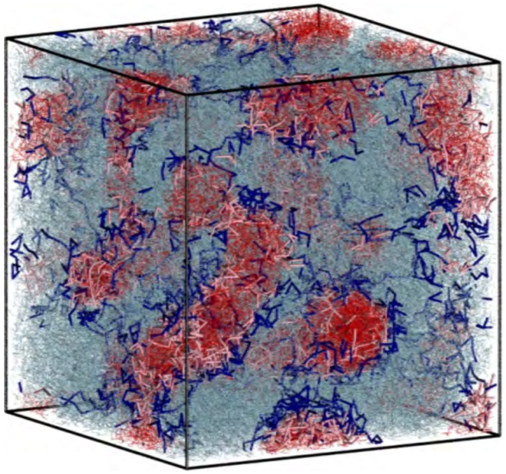
Styrene/ bromostyrene protein-like copolymer in the coil state

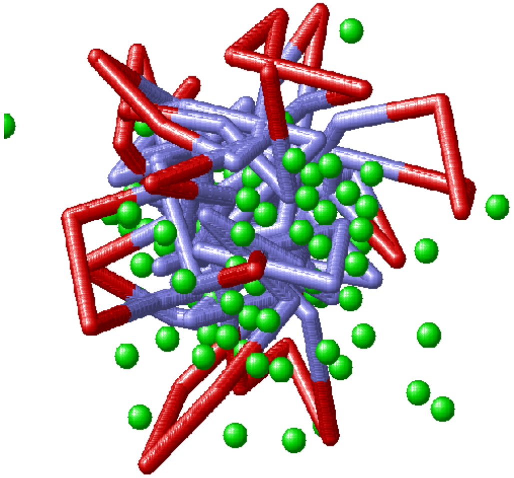
Our simulations show that protein-like copolymers are effective compatibilizers for homopolymer blends

Our Plan

- Use discontinuous molecular dynamics (DMD) and lattice Monte Carlo to explore the ability of protein-like sequences based on hydrophobically-modified chitosan to disperse oil in water







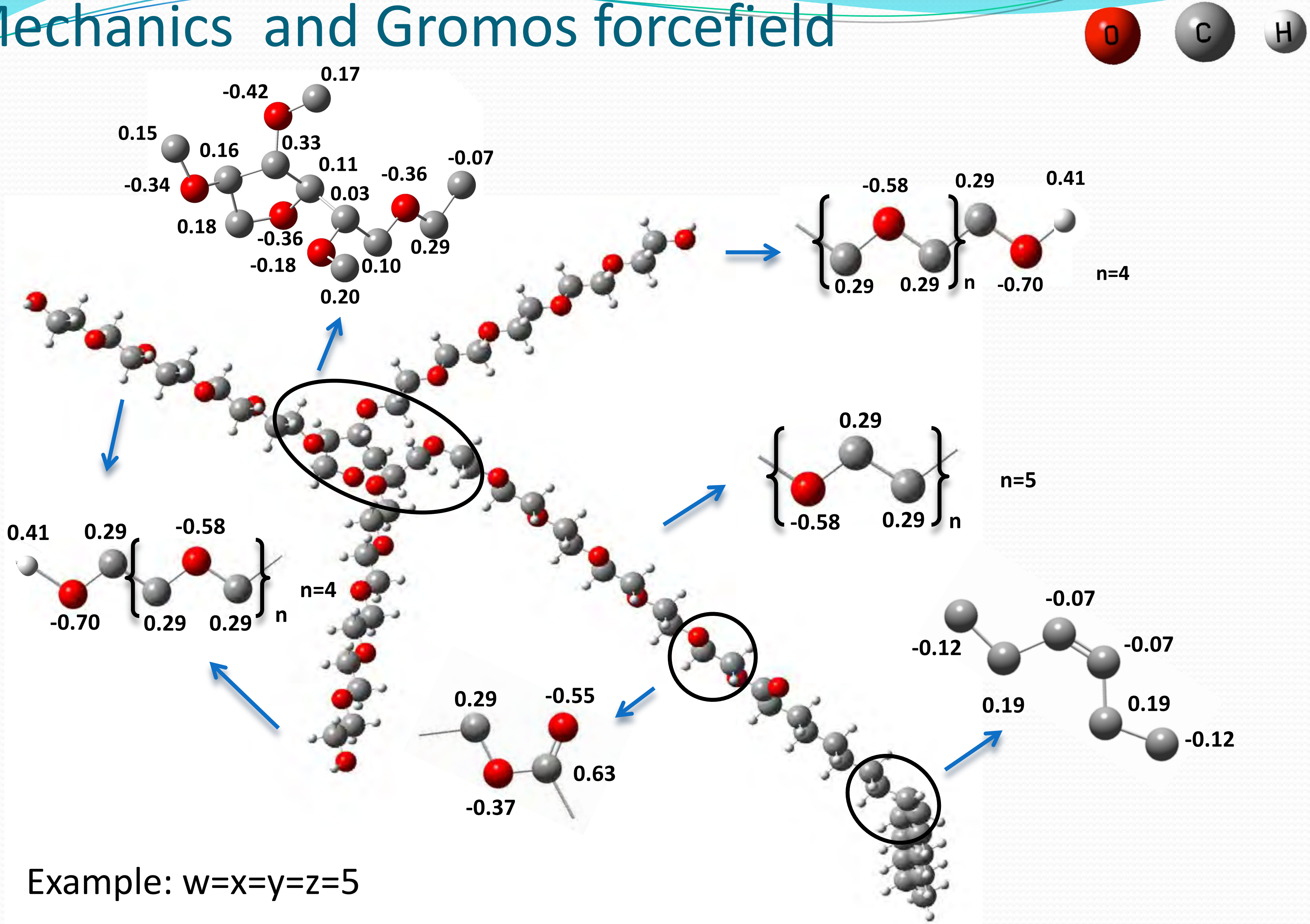
MD simulation of Tween80 and Squalane

Xueming Tang, Ronald R. Larson

Goal: Use molecular dynamics simulations to determine the phase behavior, interfacial tension, and interfacial structure for oil/brine/surfactant, both with or without dissolved gases (with Truskett and Ashbaugh)

- Gromacs 4.5.5 Molecular Dynamic simulation engine and gromos United Atom forcefield
- Partial charges of atoms are adopted from gromos forcefield, or by quantum mechanics (QM) density function method b3lyp with the basis set 6-31g(d,p)
- Intramolecular and intermolecular potentials are adopted from gromos forcefield

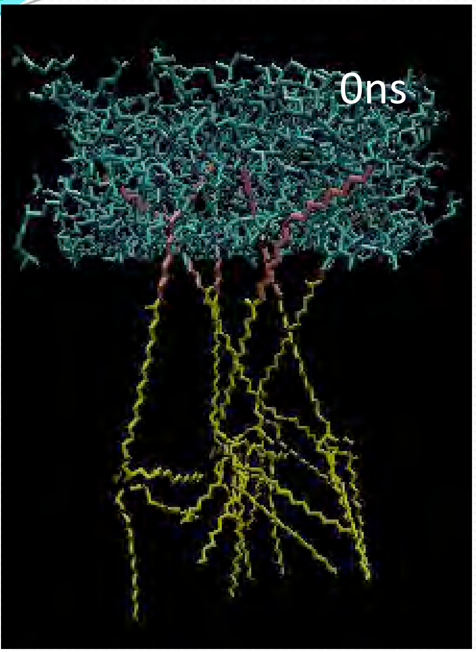
Partial Charges Estimated by Quantum Mechanics and Gromos forcefield

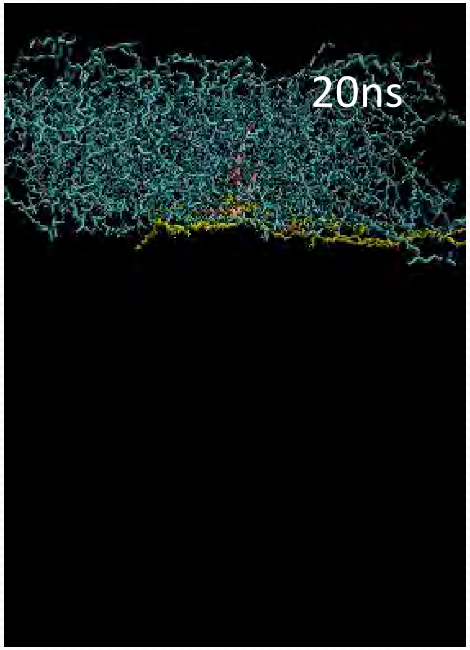


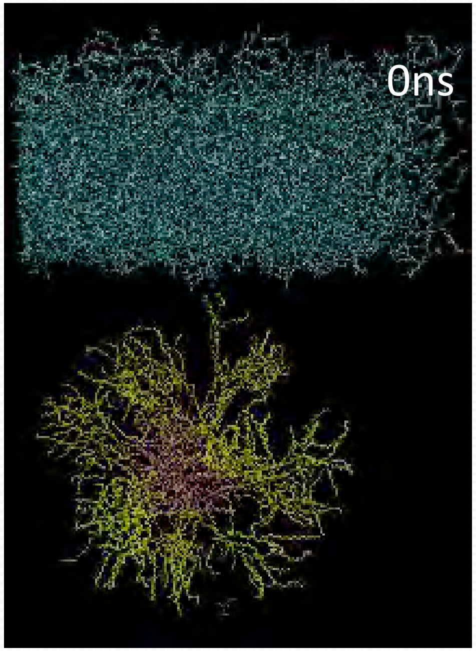
Example: w=x=y=z=5

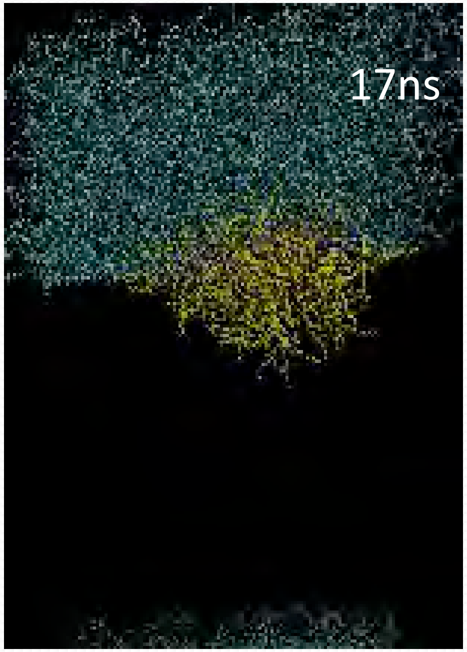
w=x=y=z=5

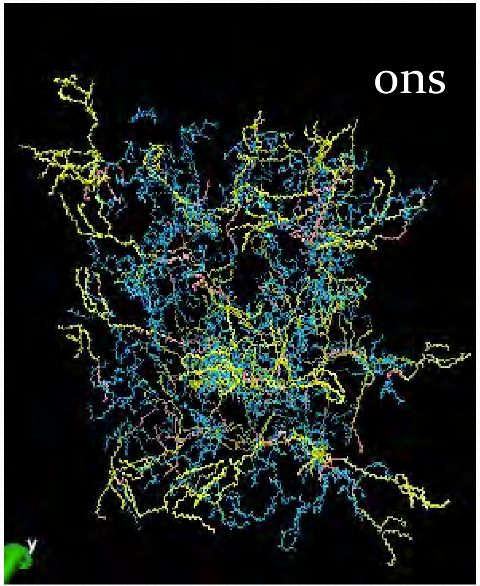
Tween 80 at interface of water and Oil

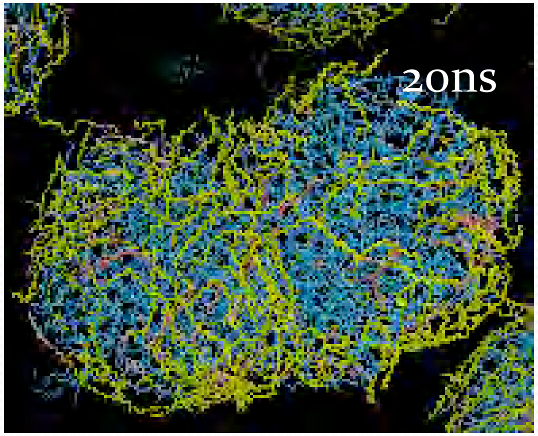












Yellow – Tween 80 head group
Pink -- Tween 80 Tail group
Blue -- Squalane (oil)
Water is omitted for clarity

Upper Left : 6 Tween 80 + 280 Squalane
Right: 60 pre-assembled Tween80 + 800 Squalane
Lower : Random distributed 60 Tween 80 + 800 Squalane

Future work & Implications

- Add additional salts to mimic sea water conditions : NaCl, $MgCl_2$, Na_2SO_4
- Apply anisotropic pressure coupling to measure Surface tension

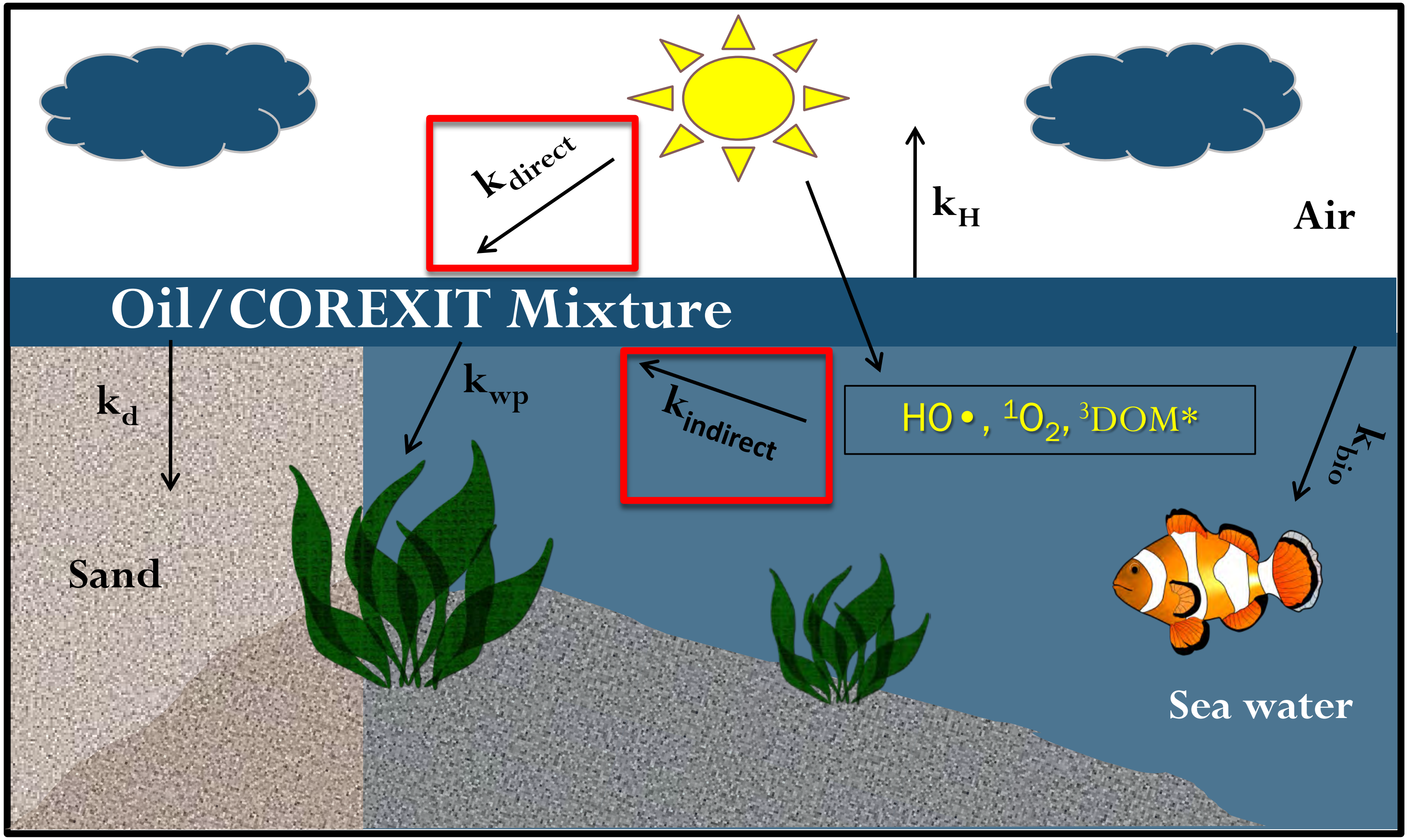
$$\gamma(t) = \frac{L_z}{2}\left(P_{zz}(t) - \frac{P_{xx}(t) + P_{yy}(t)}{2}\right)$$

- Use Martini Coarse grained forcefield to study larger scale systems
- Determine kinetics of surfactant adsorption
- Use results to estimate thermodynamic and kinetic coefficients to be used in modeling dispersant effects on oil droplet break-up

Photochemical degradation of oil dispersants in ocean and natural waters

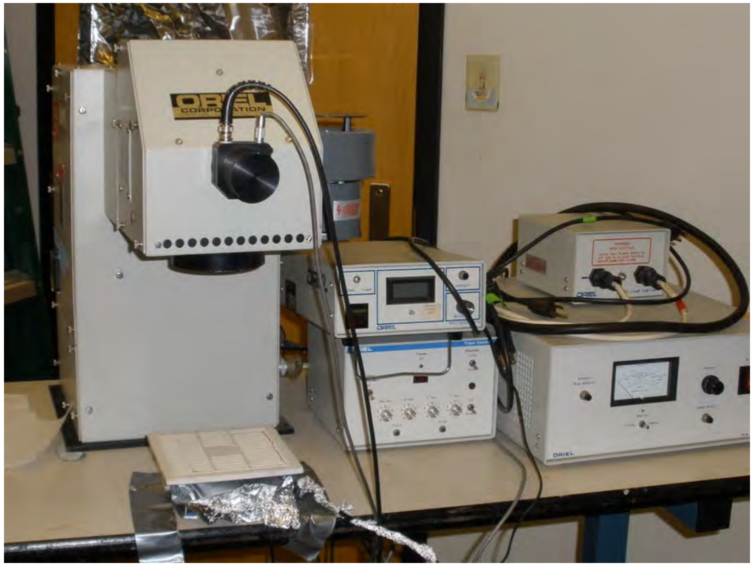
Karl G. Linden, Fernando Rosario-Ortiz, and Stephanie Kover
Department of Civil, Environmental, and Architectural Engineering
University of Colorado, Boulder

Fate and Transport Pathways



Study individual components of dispersants COREXIT 9500 and 9527A

- Ion Trap LC-MS
- GC-FID, GC/MS
- Solar Simulator
- Solid Phase Extraction (SPE)

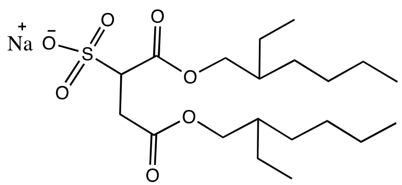
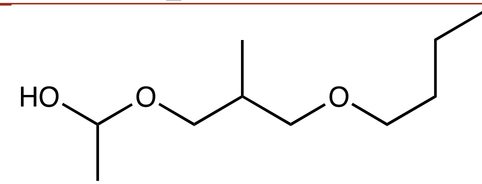


- Develop Quantum Yields
- Measure OH and other radicals rate constants
- Predict behavior under different waters and solar conditions

Results: Studied 2 compounds to date

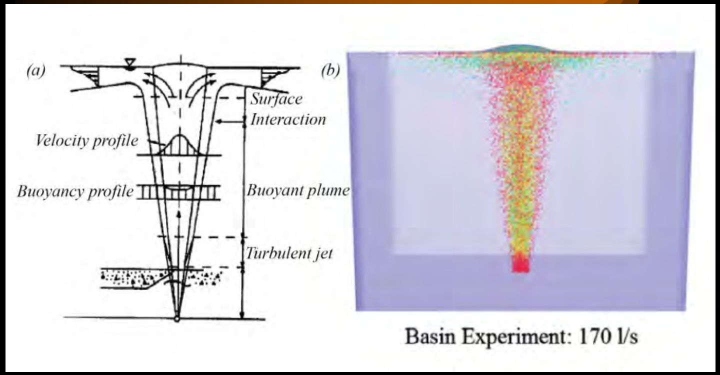
COMPOUND A: Dioctyl Sodium Sulfosuccinate

COMPOUND B: 1-(2-butoxy-1-methylethoxy)-2-propanol

Compound A	Compound B
	
$k_{overall}$ (s^{-1})	
6.90×10^{-6}	9.81×10^{-6}
$k_{HO\bullet}$ ($M^{-1}s^{-1}$)	
8.26×10^{9}	$\sim 9 \times 10^{9}$
Φ = Quantum Yield	
0.0070	0.0010

Goal: *to develop dynamic models based on CFD to capture the oil breakup processes*

- Use VOF at low Re to track detailed interface dynamics and interface mass transfer of surfactants => predict diameter, jet breakup length
- use two-fluid model to study dynamics of jets/plumes
- Use population balance models at high Re to predict droplet size distribution.



S.L. Ross Environmental Research Ltd. (1997)

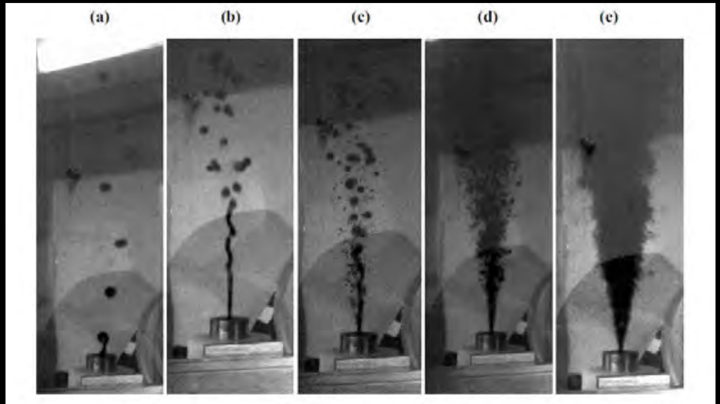
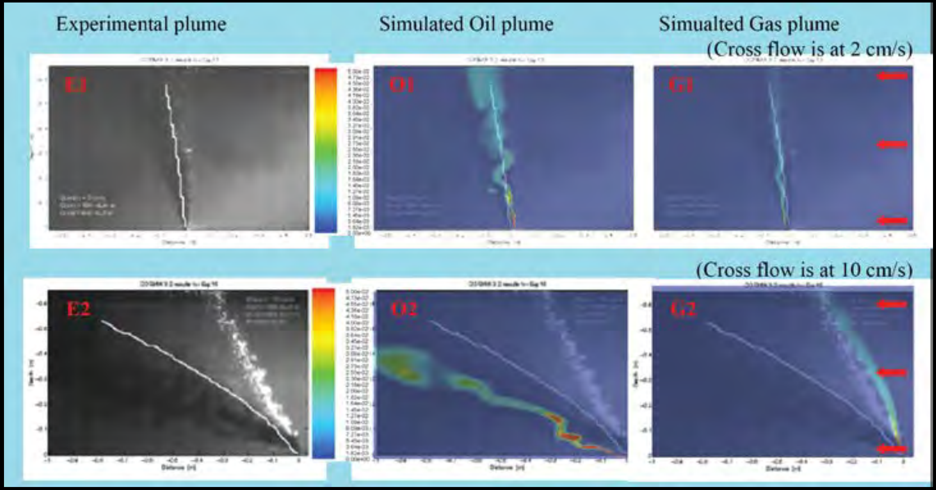
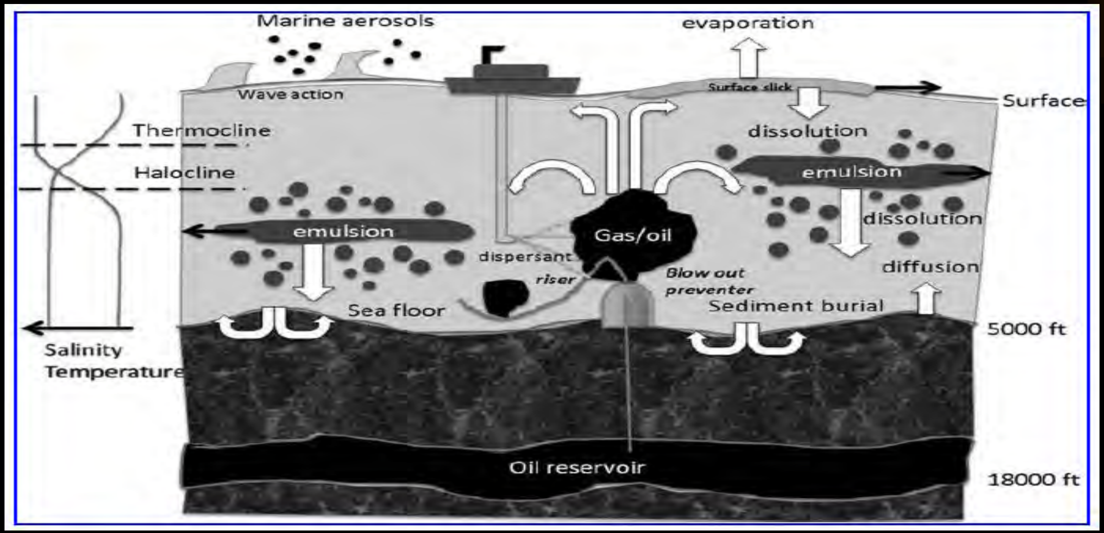


Figure III.1.1 Different modes of jet breakup observed during the oil injection experiments. Jet velocity increases from left to right. Images correspond to the case of Genesis crude oil injected into tap water at 18.1°C through a 2 mm diameter orifice. As a point of reference, the nozzle o.d. is about 2.5 cm.

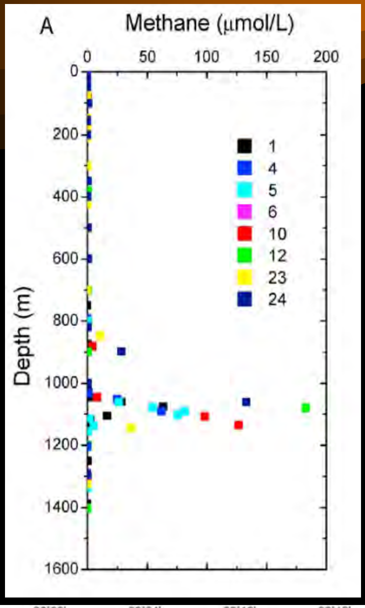
Masutani & Adams (2001), '**EXPERIMENTAL STUDY OF MULTI-PHASE PLUMES WITH APPLICATION TO DEEP OCEAN OIL SPILLS"**

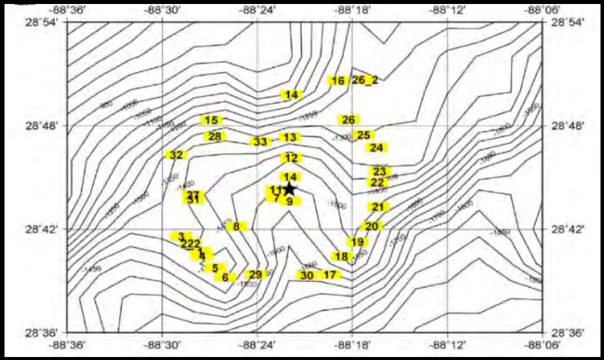


Concepts & Physical principles



Thibodeaux, L. J., K. T. Valsaraj, et al. (2011). Environmental Engineering Science **28**(2): 87-93.



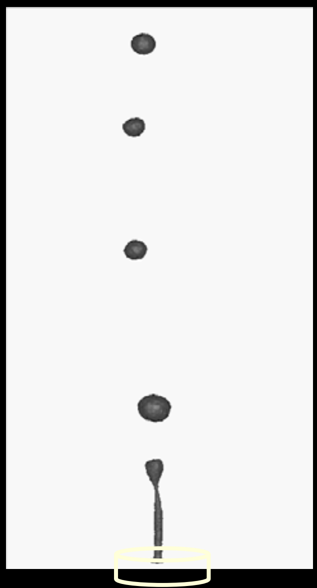


Yvon-Lewis, Hu et al. (2011)

Involves a complex set of physicochemical processes

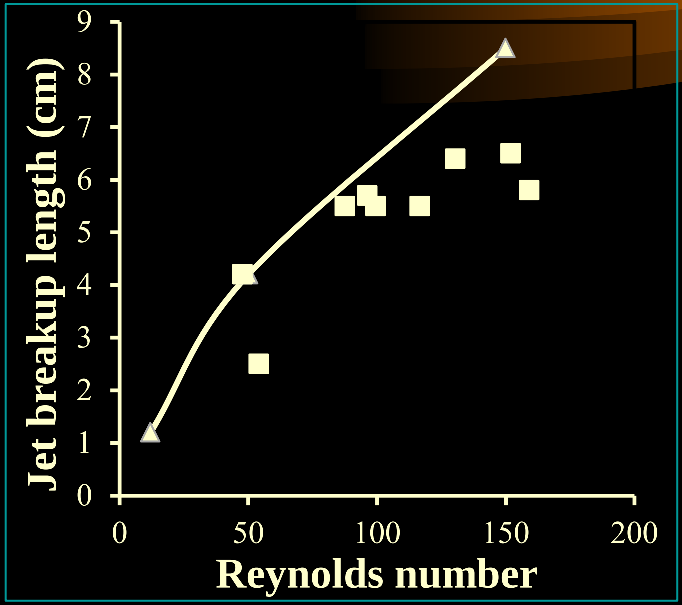
- Significant gas release (in GoM - GOR is 2380)
- Hydrate formation
- Dissolution of lighter material followed by sinking
- Intrusion layer formation in stratified fields
- Advection of gas and oil at different rates
- Surface evaporation (followed by sinking?)

Preliminary simulation results

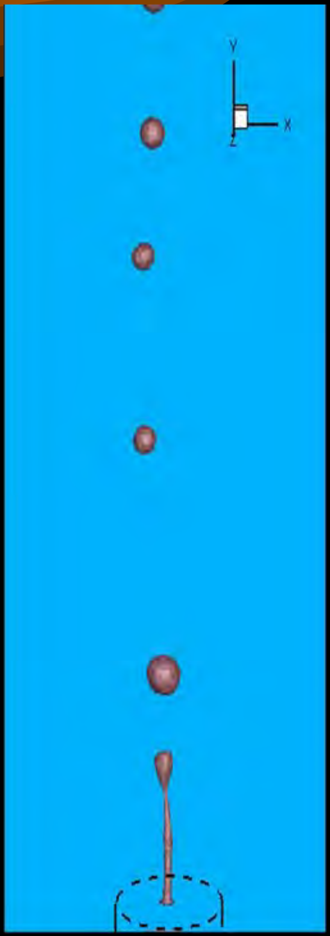


CFD Simulation
Crude oil
Re = 18

Experiments Masutani and Adams(2000)
Crude oil, Re = 20



— CFD; ■, Experiments Masutani and Adams(2000)

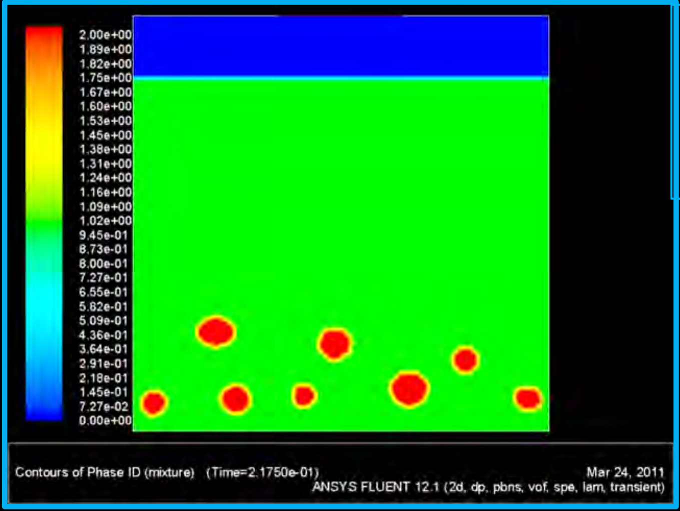


Reynolds number is based on nozzle diameter and properties of the crude oil

Experimentally observed average size of the oil drop lets is 7. 5 mm.
The simulated oil droplets after jet break up is 8.1 mm

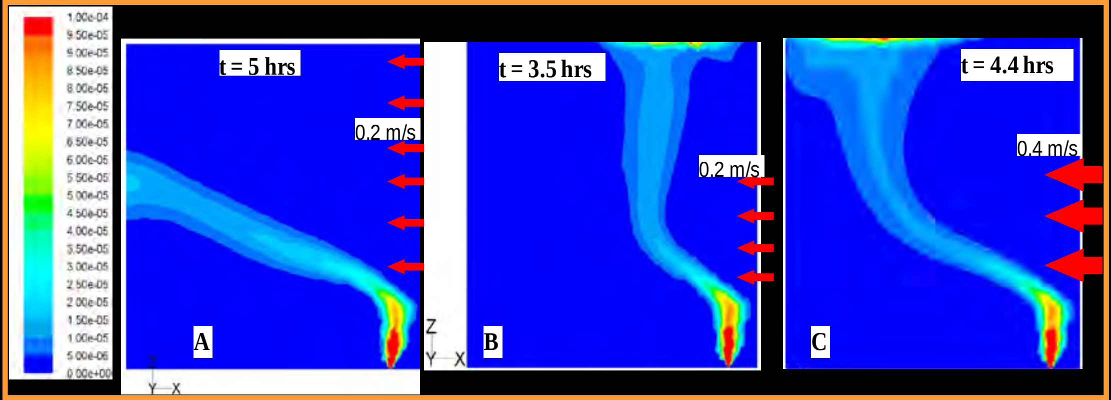
Implications of work

Can shed light on the forces that determine the fate of the hydrocarbons



High fidelity (DNS-VOF) model captures dissolution while rising in water and evaporation on the surface followed by sinking to the ocean floor.

Low fidelity (TFM) model captures plume dynamics and its interaction with the ocean currents.



Predicting the diameter of droplet/bubbles is crucial. It determines the residence time, hence the amount of dissolution of the light material and hence the ultimate fate of the droplets.

Dispersant-Assisted Motility of Bacteria in Porous Media

Kyriakos Papadopoulos
Tulane University

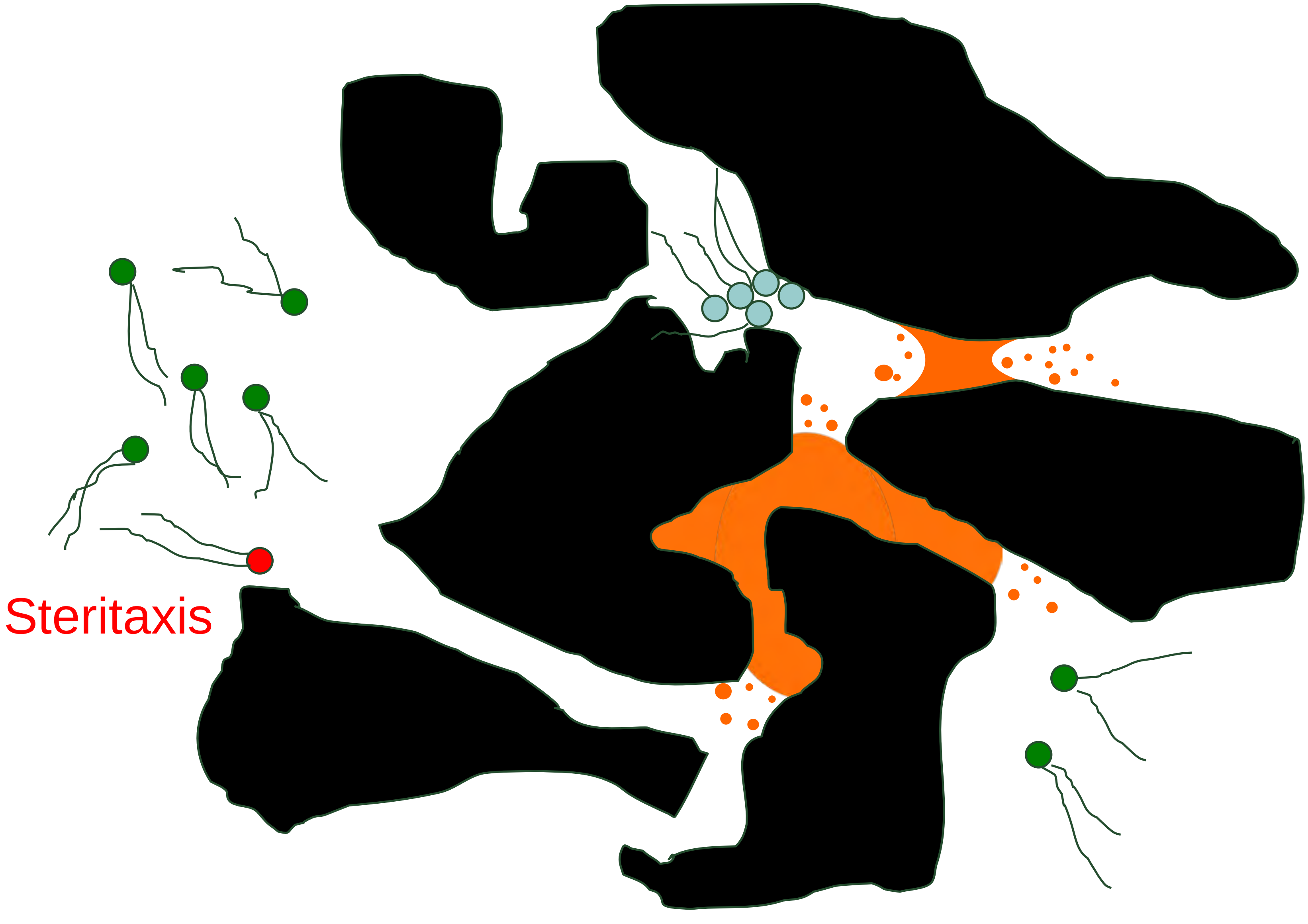
Objective: Determine and control the response of bacterial swimming to dispersants in porous media

More specifically,

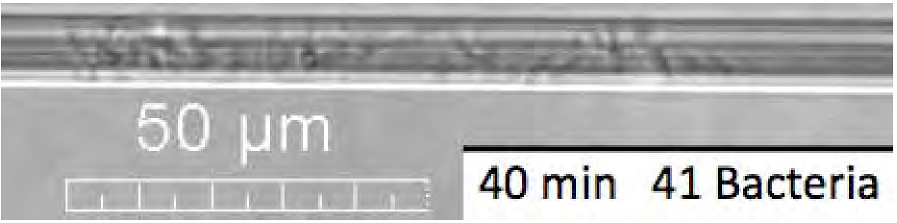
Prevent: aggregation – biofilm formation – pore clogging

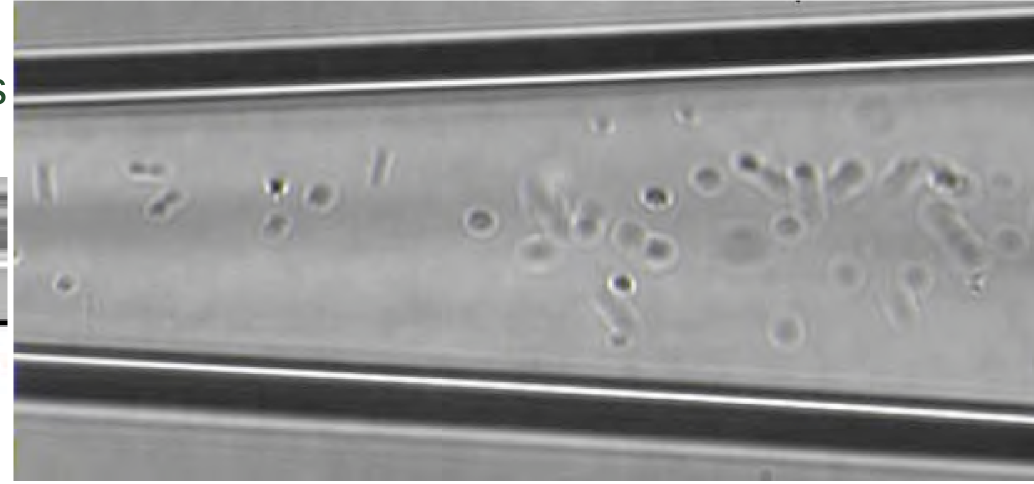
Facilitate and promote: unidirectional and steritactic swimming

Concept and physical principles

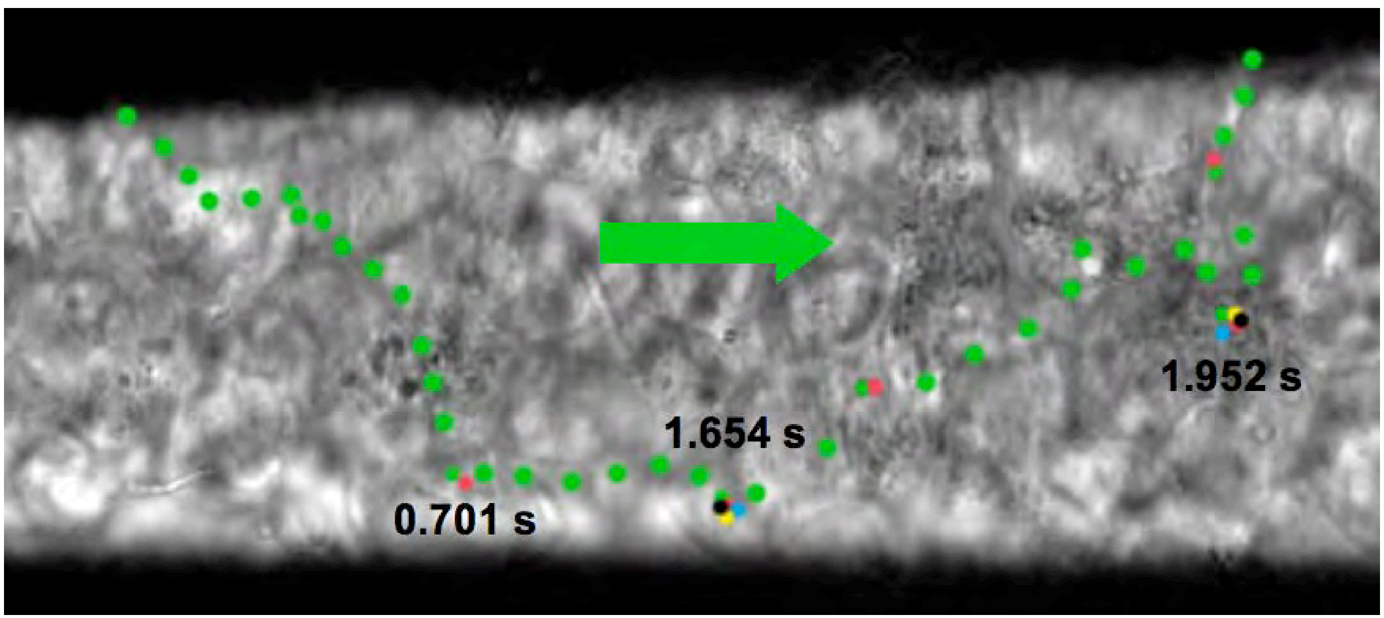


Steritaxis in Tapered (Conical) Capillaries

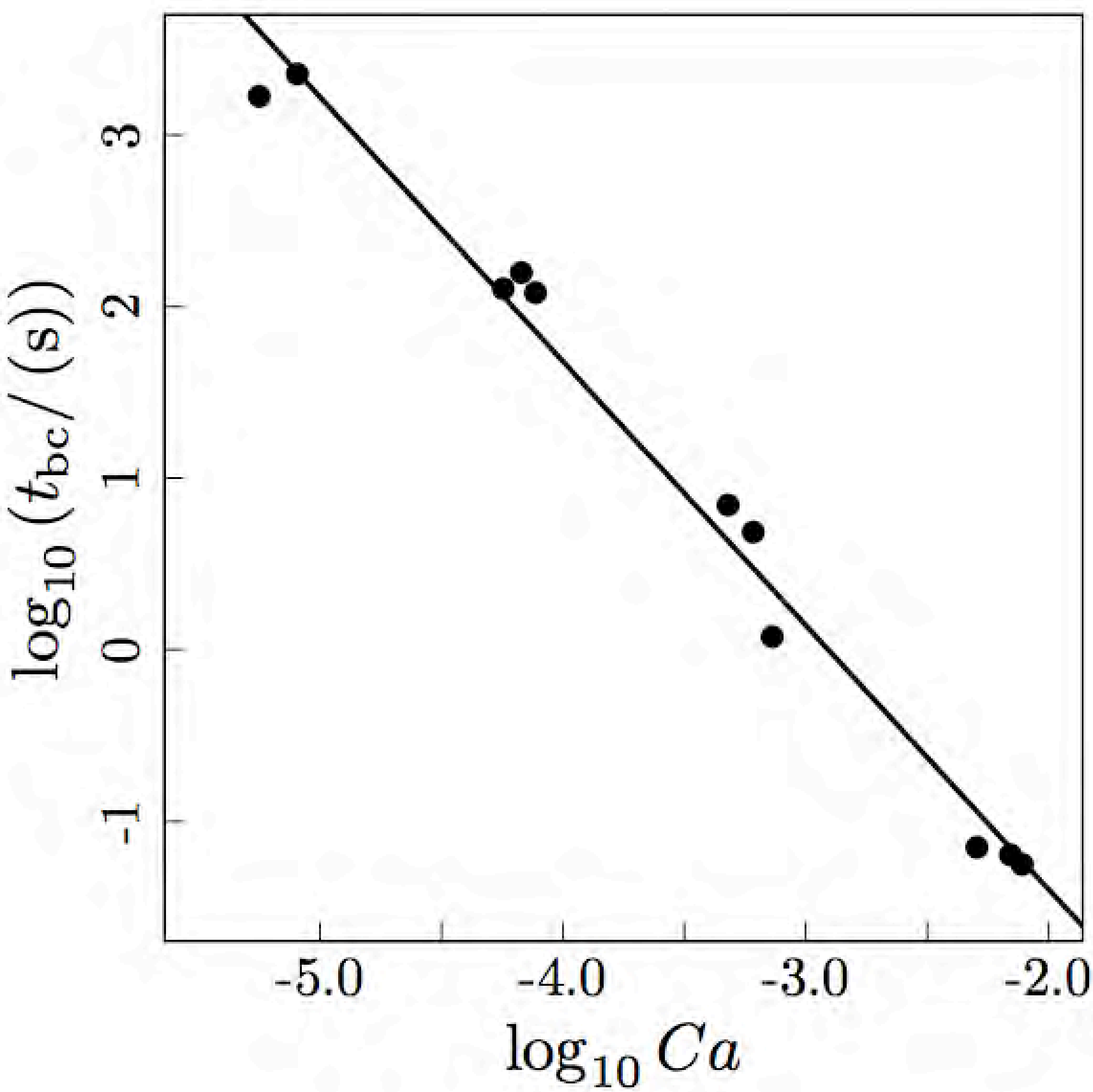




Steritaxis in Transparent 3-D Random, Natural Porous Media in Capillary Packed Beds



Breakthrough time as a function of capillary number Ca



Interaction of Oil droplets with Wetland plant life

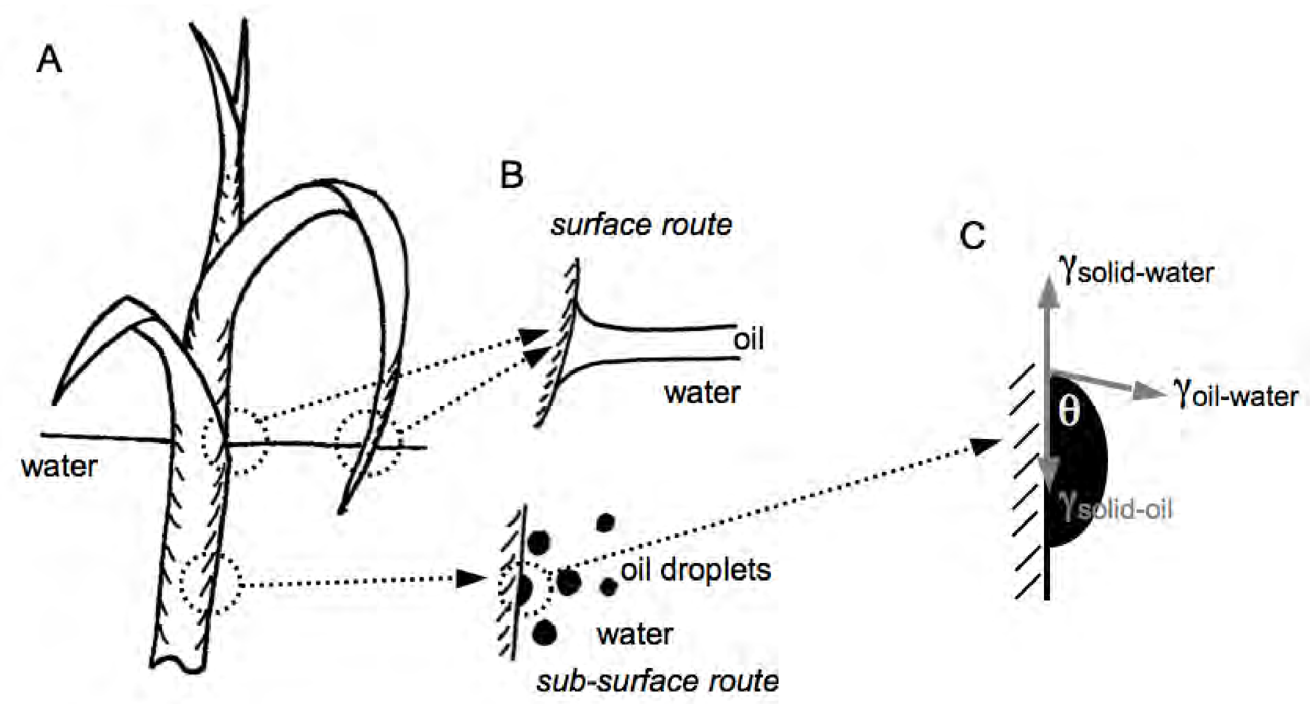
Noshir S. Pesika

Chemical & Biomolecular Engineering Department

Tulane University

New Orleans, LA

Goals

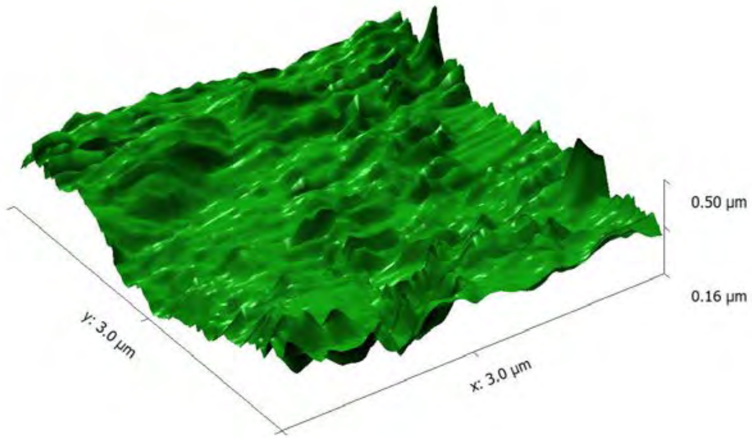


(1) Understand the interaction of oil droplets with wetland plant life
(2) Identify new dispersant formulations based on block copolymers and/or pickering emulsions to enhance the stability of dispersed oil droplets

Preliminary Results

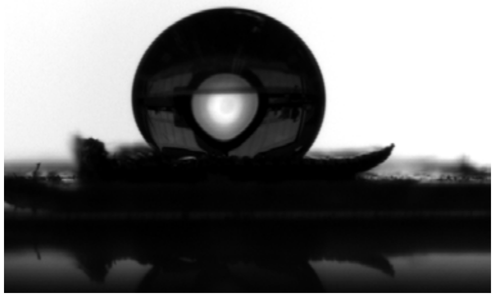
Mimicking a leaf (Spartina alterniflora) surface

Topography



AFM image of the top surface of a leaf.
RMS ~50 nm

Surface energy



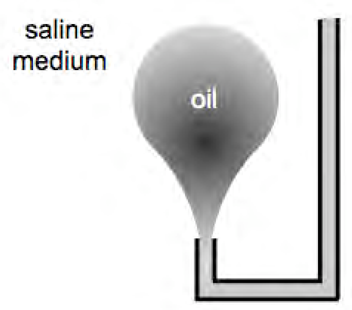
Static contact angle measurement using a water drop.
Contact angle ~135^{o}

Future plans: Interaction between Oil and Surfaces

New dispersant formulations based on pickering emulsions and block co-polymers

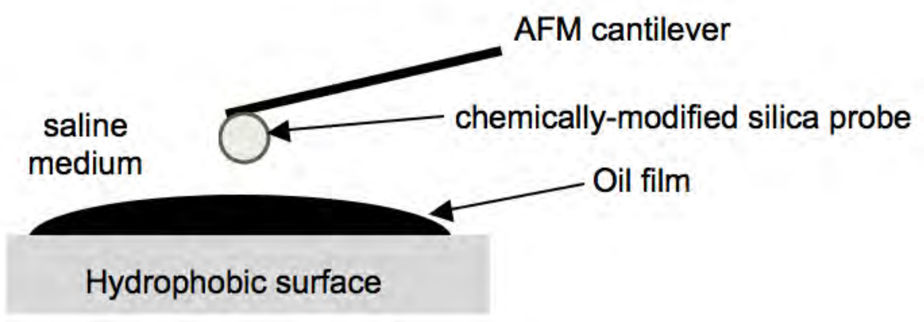
Pendant drop measurements

- Dynamic and equilibrium surface tension



AFM force measurements

- Distance-force curves



Microfluidic studies of dispersion and coalescence

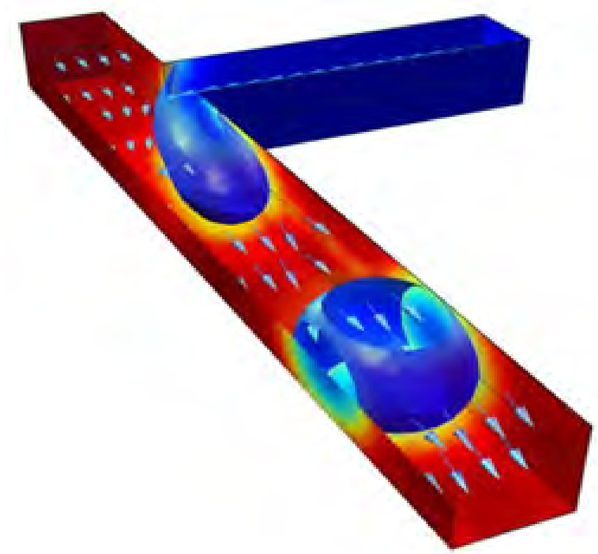
Robert K. Prud'homme & Howard A. Stone:
Princeton Univv.

Technical Goal: Understand the optimal surfactant and polymeric surfactant combinations to enable rapid dispersion of oil in the deep water environment, but stabilization against coalescence at the ocean surface.

Scientific Goal: (1) Understand rapid kinetic processes involving adsorption of small (surfactant) and large (polymers) species on oil/water interfaces using microfluidics. Develop the microfluidics tools to study these processes on faster times scales than has been previously possible. (2) Understand long time kinetics of desorption/deprotection of liquid interfaces using ultracentrifugaiton.

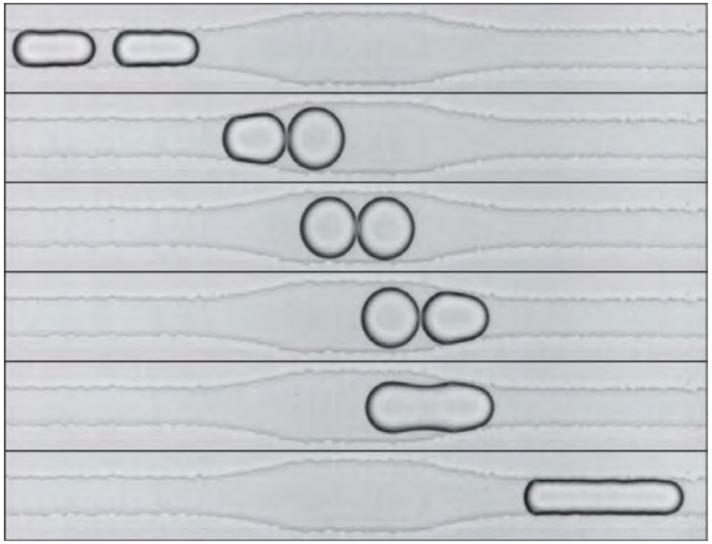
Microfluidics for sub-millisecond drop breakup

1. *Microfluidics enables ultrafast studies of surfactant attachment to interfaces and drop breakup.*
2. *The drop breakoff problem mimics oil dispersion where surfactant and flow disperses oil.*
3. *Microfluidic geometries enable drop breakup frequencies O(kHz). The rules for constant surface tension, immiscible fluid breakup are known. By introducing surfactant and amphiphilic polymer solutions “effective” interfacial tensions can be determined.*
4. *Interfacial Fluorescent Radiative Energy Transfer (FRET) measurements are being pursued to directly measure surfactant arrival on the interface at sub-millisecond time scales.*



Microfluidics for rapid and controlled coalescence studies

1. *In the initial dispersion event the prevention of re-coalescence is required.*
2. *A novel microfluidics geometry enables drop generation and contact over time scales of sub-second . The forces of contact are known quantitatively.*
3. *The surfactant/polymer protection of the interface against coalescence will be studied.*

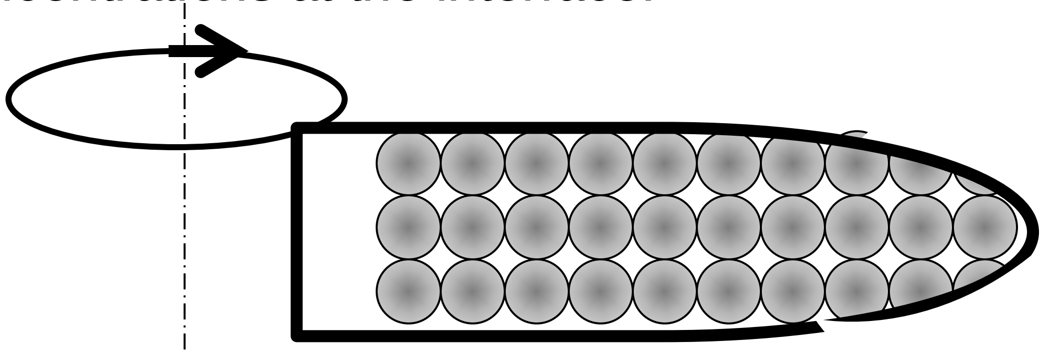


Lai, A.; Bremond, N.; Stone, H. A. *Journal of Fluid Mechanics* **2009**, *632*, 97.

Bremond, N.; Thiam, A. R.; Bibette, J. *Physical Review Letters* **2008**, *100*.

Ultracentrifuge studies of long-time stability

1. *When oil rises to the surface it is desirable to prevent coalescence into a "slick". During the slow rise to the ocean surface the partitioning of surfactants off of the interface can lead to unstable drops and coalescence. Polymers are more resistant to displacement.*
2. *Model monodisperse emulsions made using microfluidics will be dialyzed to allow surfactant displacement.*
3. *Ultracentrifugation will be used to impose known forces, image analysis of coalesced drops will be used to assess coalescence and stability.*
4. *Fluorescently tagged polymers will enable measurement of polymer concentrations at the interface.*



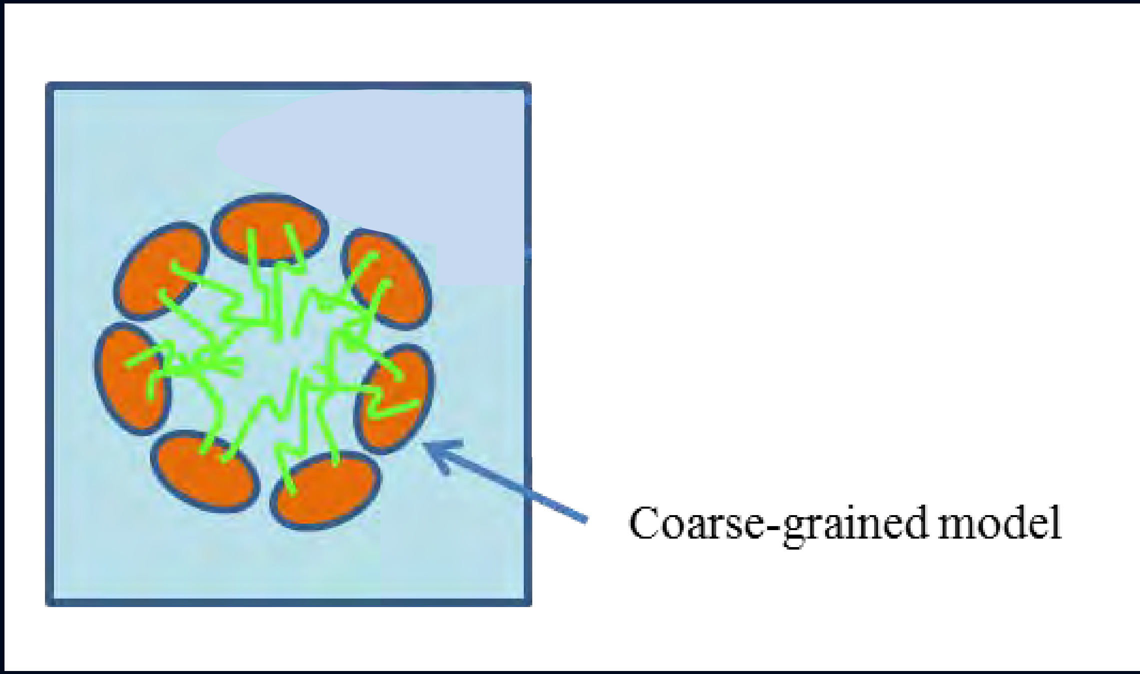
Current status

1. *Chris Chen, a first year graduate student from Stanford, has joined the project.*
2. *The microfluidics device (tee junction) has been fabricated and tested*
3. *Fluorescent FRET pairs are being synthesized to to study surfactant concentration at interfaces with sub-millisecond resolution.*

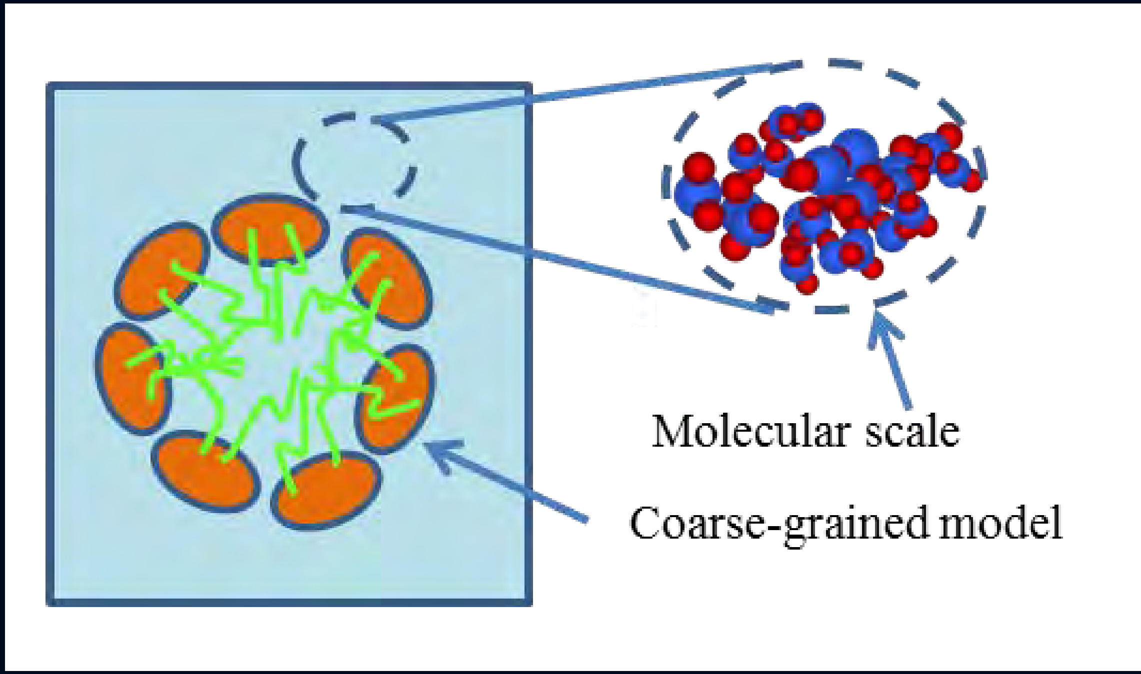
Equilibrium dispersant behavior relevant to deep-sea water conditions:

Coarse-grained approaches for modeling effects of low temperature, high pressure, and high salt concentration

TM Truskett, *The University of Texas at Austin*



What's essential for modeling phase behavior, CMCs, interfacial tension, etc.?



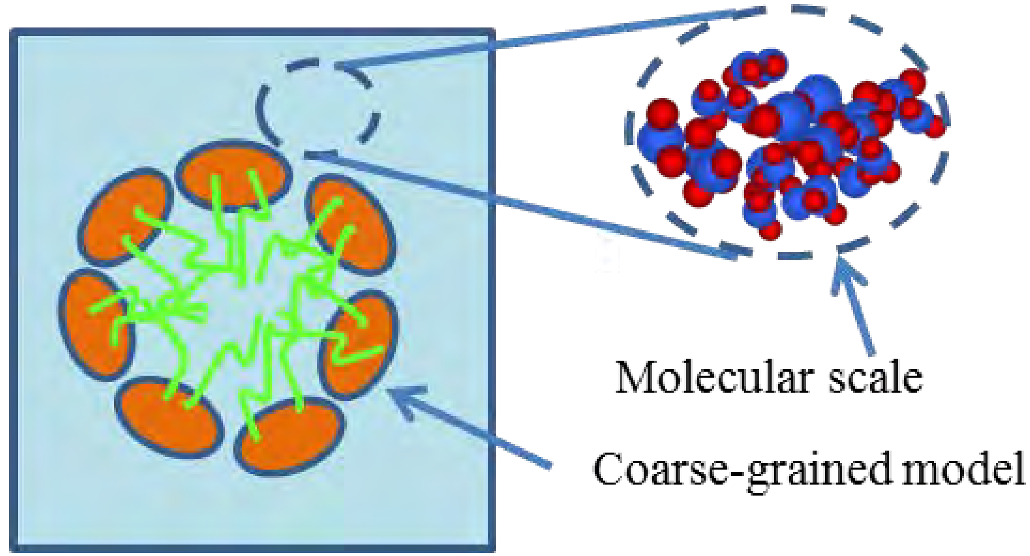
What's essential for modeling phase behavior, CMCs, interfacial tension, etc.?

-viable multi-scale strategy
-adequate "effective" description of water

Coarse-graining approaches:

(1) Simulation-based strategy based on molecular-scale correlation functions

(2) Molecular-thermodynamic theory



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Research activities

Theory

Extend molecular thermodynamic approaches of

- Jusufi et al., *J. Phys. Chem. B,* 2012 &
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Simulations

Develop and explore the state-point sensitivity of coarse-grained models for dispersants via

Allen & Rutledge, *J. Chem. Phys.*, 2009.

Implications

Practical

New tools for predicting properties of dispersants in water for conditions relevant to deep-sea releases

Properties can help to design new dispersants and provide data needed for continuum models

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Fundamental

New understanding of hydration and assembly processes in aqueous media

Stringent tests that will help to develop and improve coarse-graining strategies

Atmospheric Transport of Oil and Dispersant Components By Aerosolization from a Deep Sea Oil Spill

Franz S. Ehrenhauser, Paria Avij, Victoria Dugas, Isaiah Woodson, Kalliat T. Valsaraj

Cain Department of Chemical Engineering

Louisiana State University, Baton Rouge, USA

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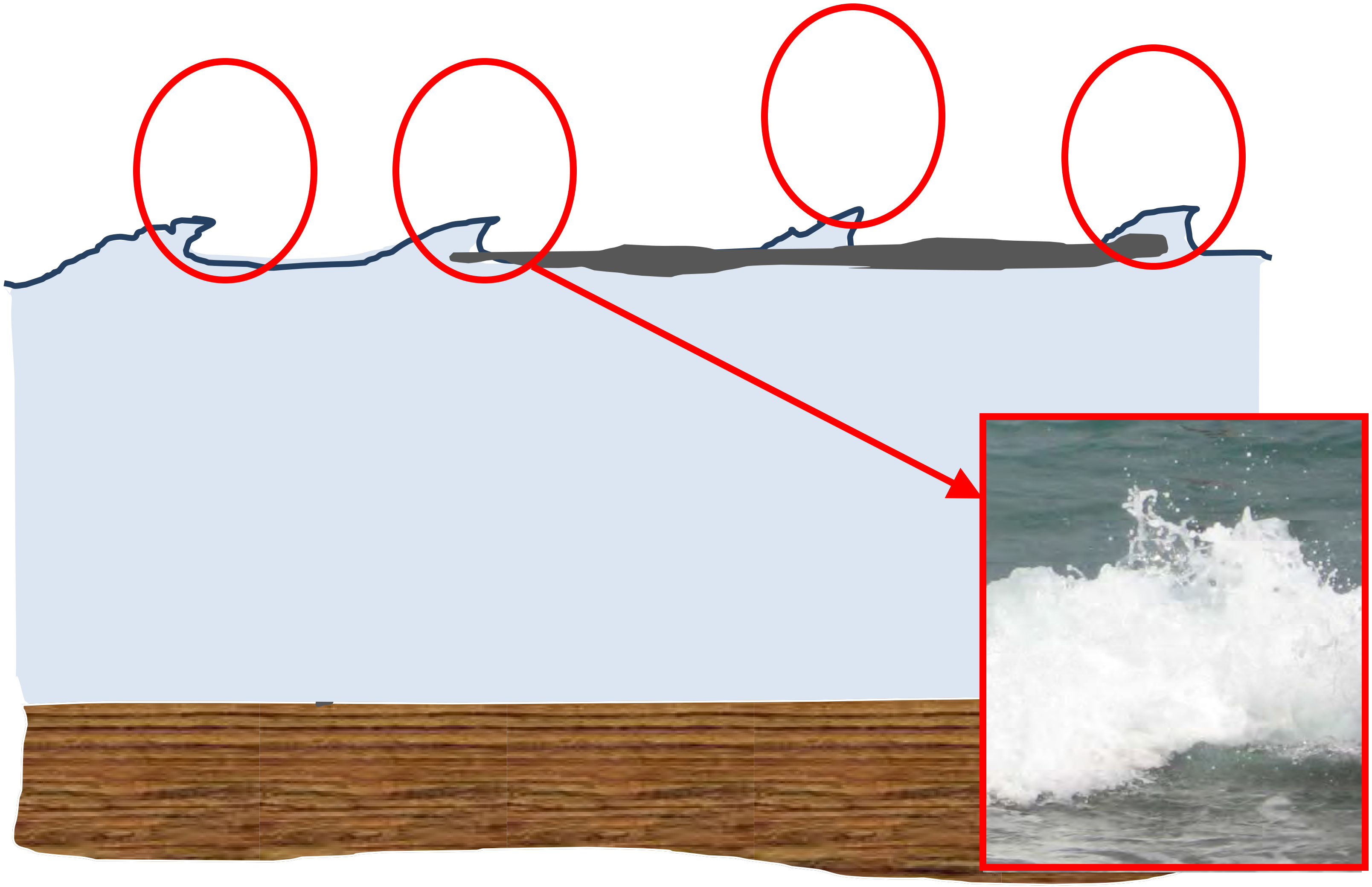
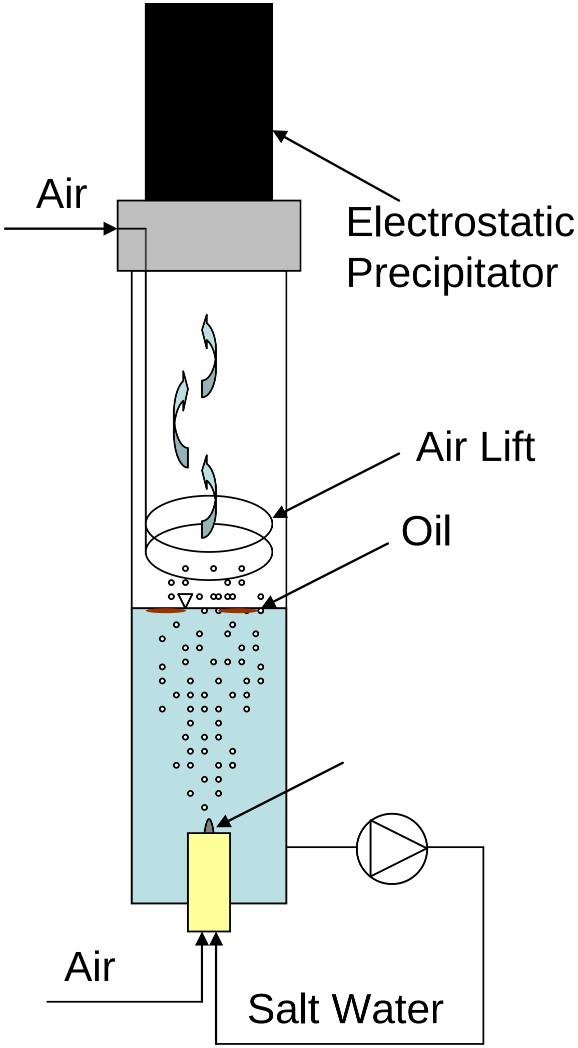
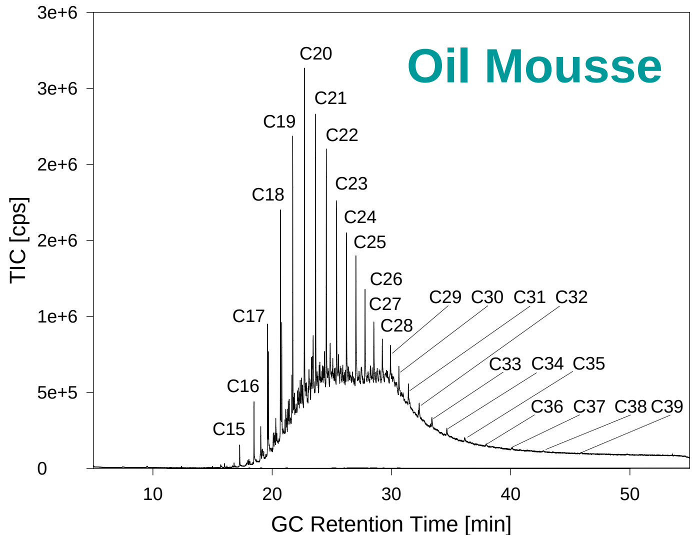


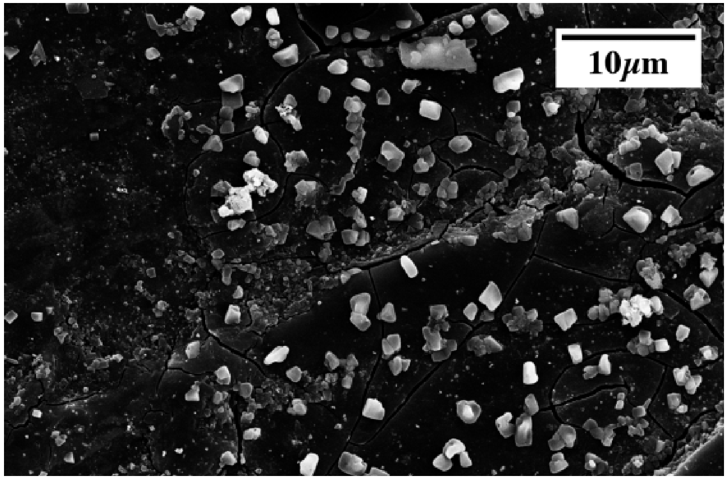
Methods

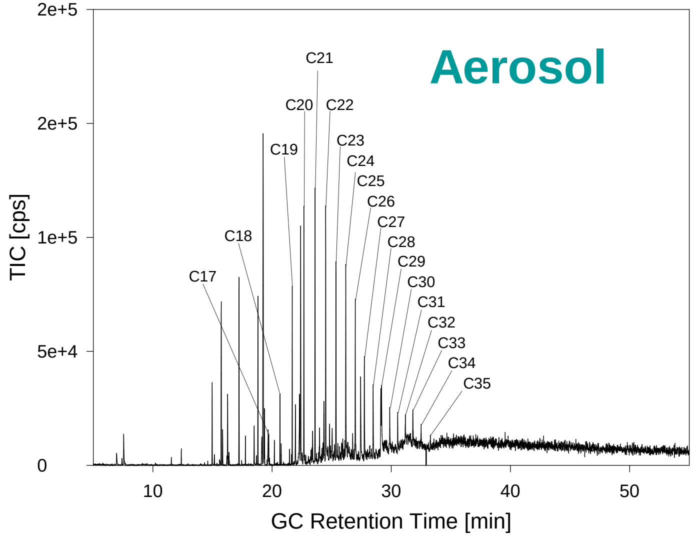


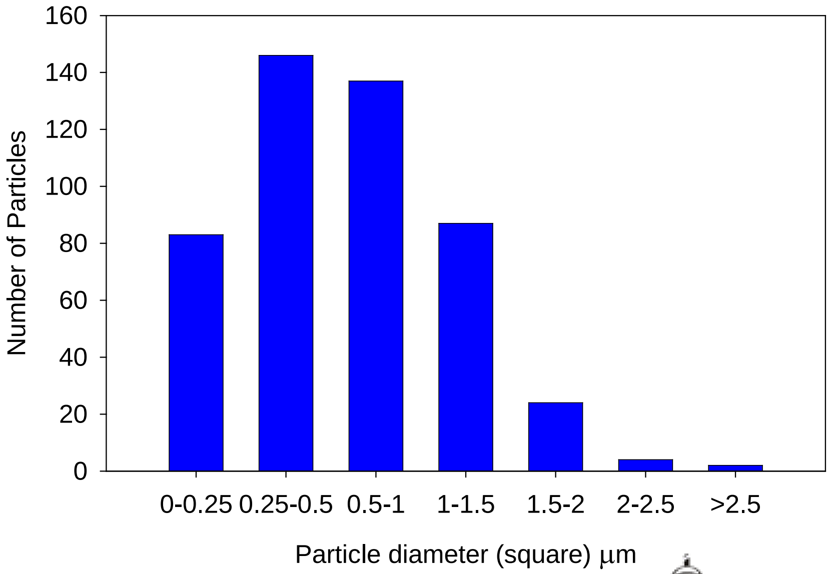
- Aerosol generation via bubble column reactor
- GC-MS (GC-FID) analysis of oil spill matter and generated aerosol
- Characterization of generated aerosol particles via GC-MS, SEM,

Preliminary Results









Proposed Work

- Evaluation of the generated **aerosol** via bursting bubbles in the presence and absence of **surface active compounds**
- Evaluation of the **aerosolization of oil spill matter** (source/surface oil and aged oil) in the presence of dispersants
- **Dispersants** to be tested: Corexit 9527, Corexit 9500, Dispersit, anionic, nonionic and cationic surfactants
- More: Wednesday, March 28, 2012 06:00 PM
  ENVR General Posters