Thermodynamic and Kinetic Pathways to Emulsification

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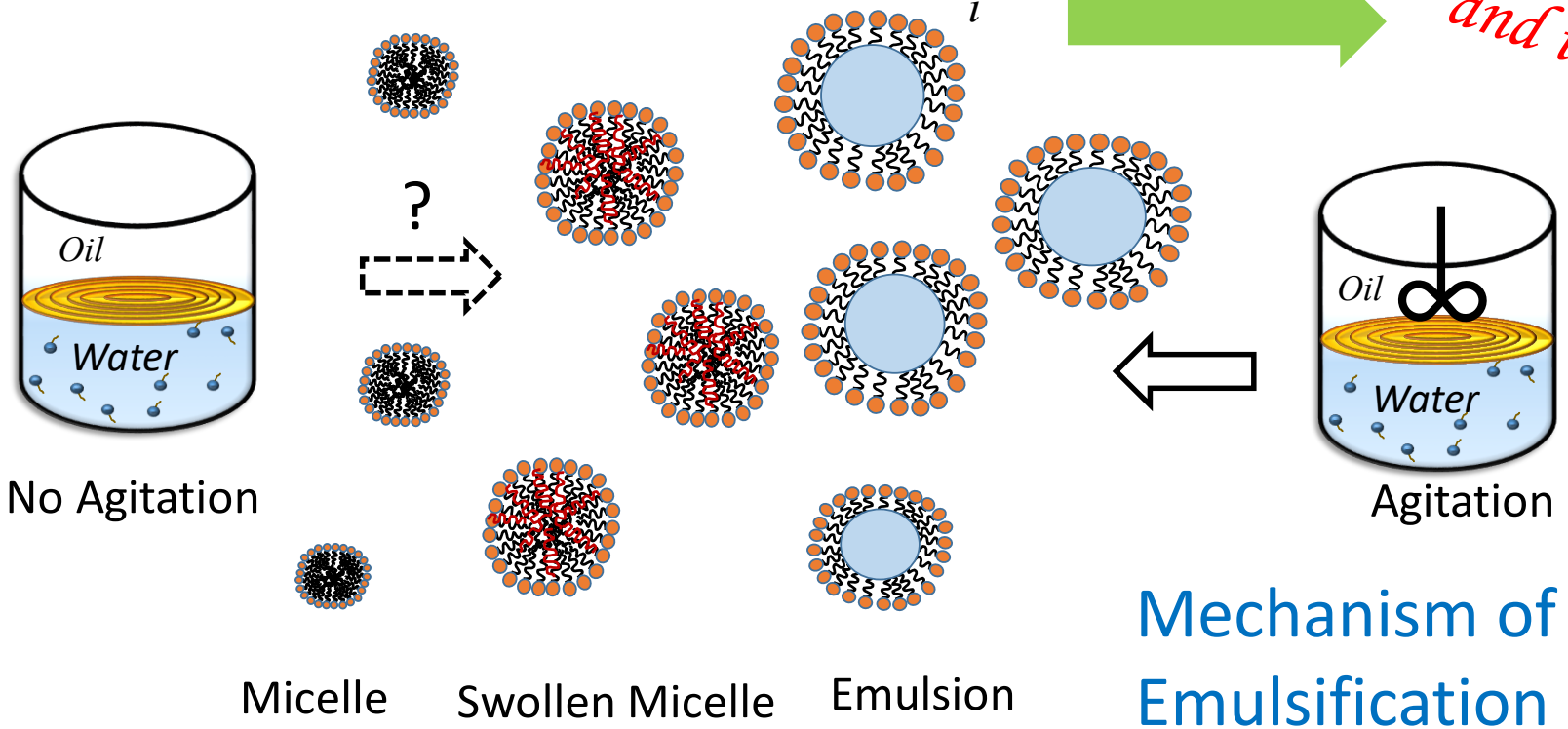
25 YEARS OF ESTCP
2019 | Enhancing DoD's Mission Effectiveness

Conventional Wisdom of Emulsification

Total Surface Free Energy Increases $\sum_i \gamma_i A_i > 0$

We start First from right to left and then from left to right



Baker, Florence, Tadros, and Wood, JCIS (1984)

Langevin, Annu. Rev. Phys. Chern. 1992

Mechanism of Spontaneous Emulsification is not Understood

$$for \quad \gamma_i > 0$$

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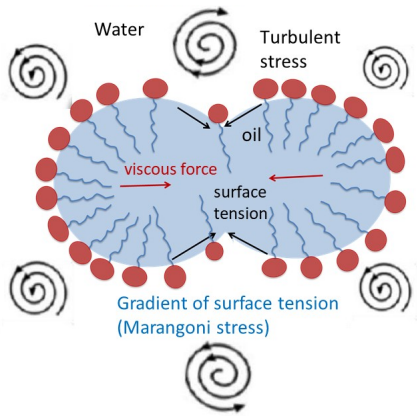
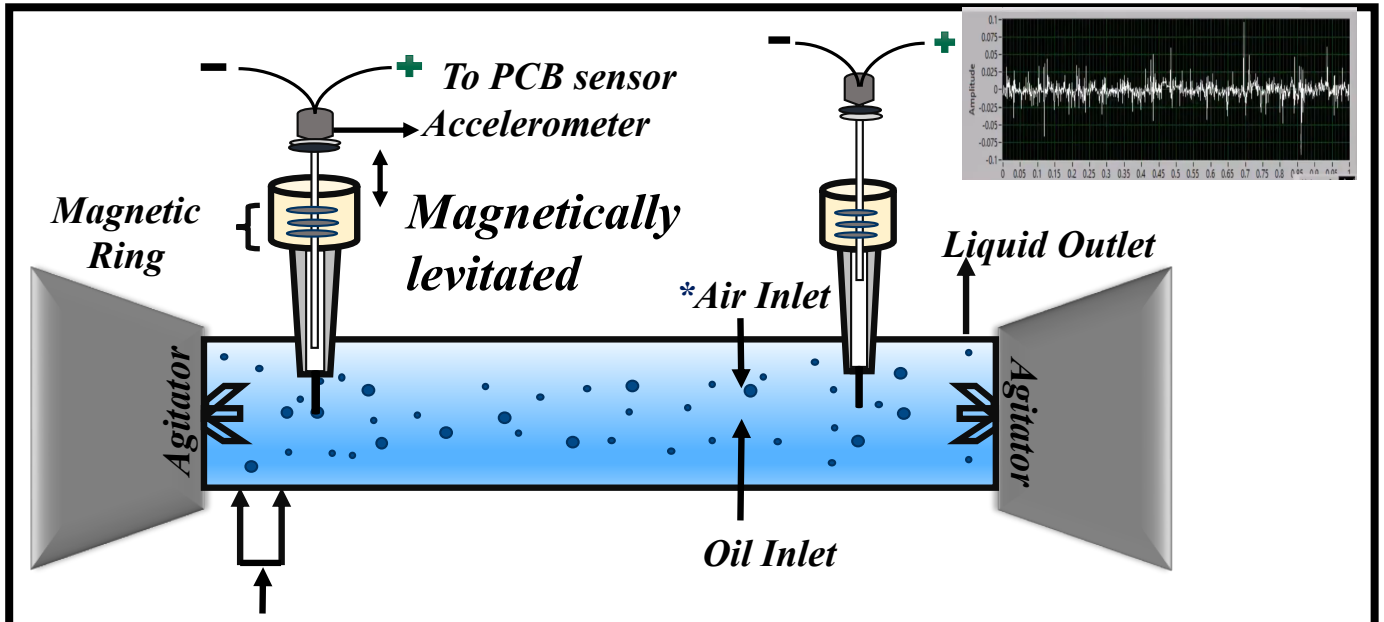
Revisit Emulsification with Agitation



Droplet Radius is obtained by balancing Laplace Pressure with Fluctuating Pressure

Danov, et al *JCIS*, **1994**



* *Air Tight: Experiment can be done under air free condition*

* *Air can be injected when needed*

Nominal power input = voltage x current

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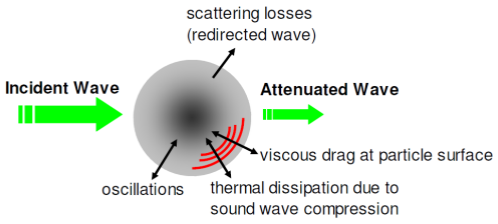
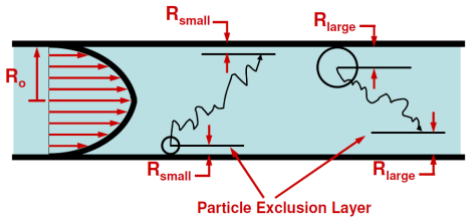
Droplet Size Analysis





- Acoustic Impedance Spectroscopy (APS) (10 nm to 40 micron)
- Capillary Hydrodynamic Fractionation (CHDF) (5 nm to 1000nm)
- Microscopy (Including Epi-Fluorescence, Brownian Motion Microscopy)

Coupled with

UV-Vis Spectroscopy

Thermo Scientific™ NanoDrop™ One^{C} Microvolume UV-Vis Spectrophotometer

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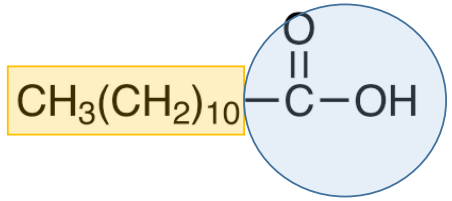
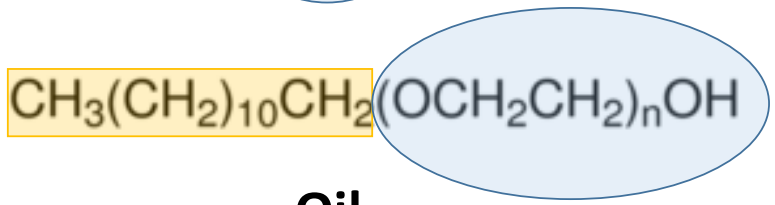
Composition of Emulsion

Surfactants

Dodecanoic Acid



Brij 35 (non-ionic)



Oil

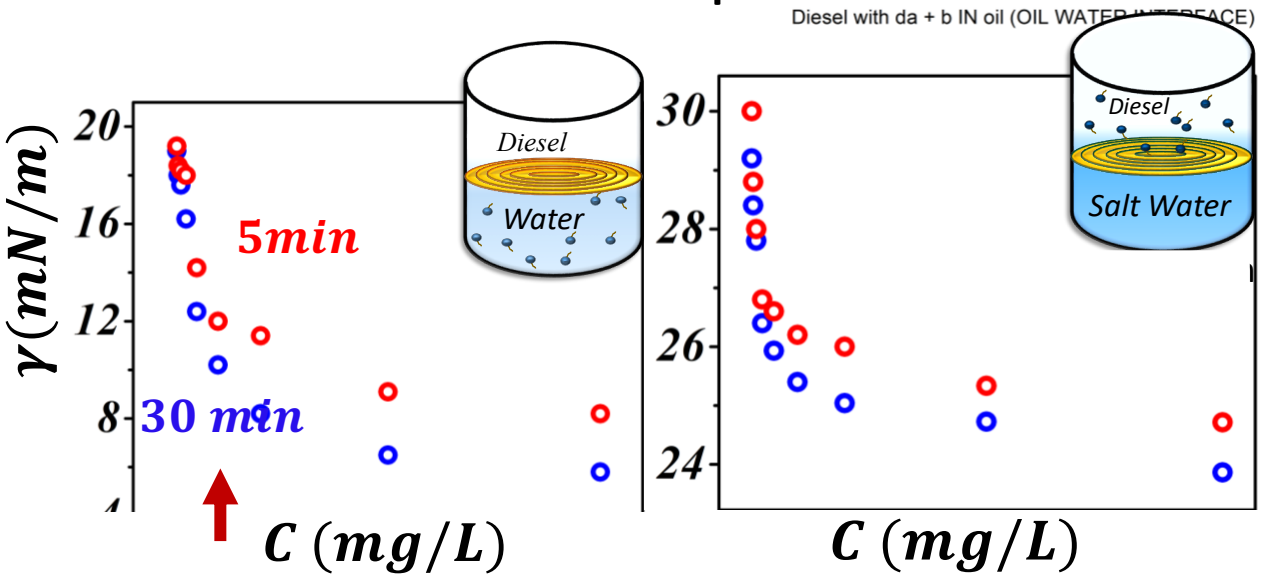
Heptane, Dodecane, Diesel (chromatographed), Texas Crude Oil (with natural surfactants)

Salt Water

(0.6 M NaCl, pH~ 7)

Interfacial Tensions measured for various combinations (surfactants and their mixtures), added in oil or water

An Example



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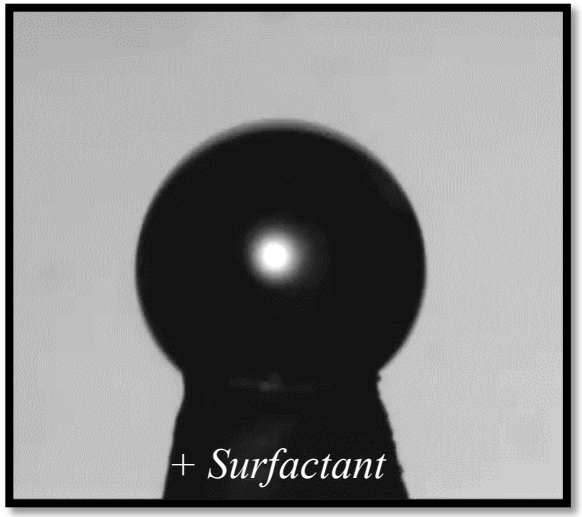
Drop resonance: a way of measuring Surface Tension

- Usually Static Interfacial Tensions are Measured, which we use
- Dynamic Interfacial Tensions Can also be Measured using Standard Methods

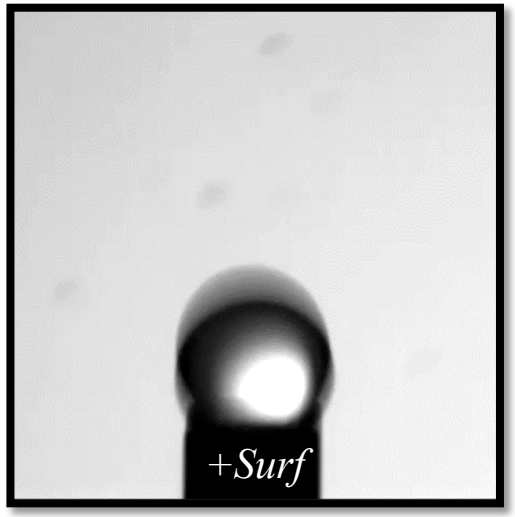
For High Frequency (>100 Hz)

Fast internal mixing helps to reach end point quickly

In Air



In Heptane



$$\omega \propto \left(\gamma / \Delta\rho V\right)^{1/2}$$

Mettu and Chaudhury, Vibration spectroscopy of a sessile drop and its contact line, Langmuir 2012

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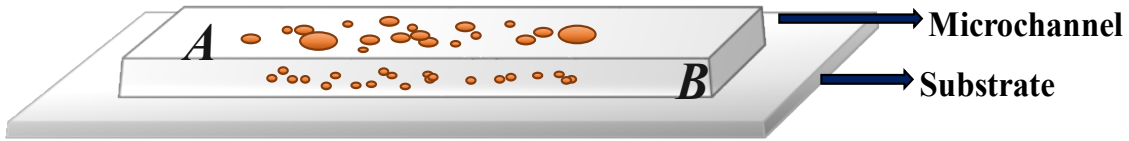
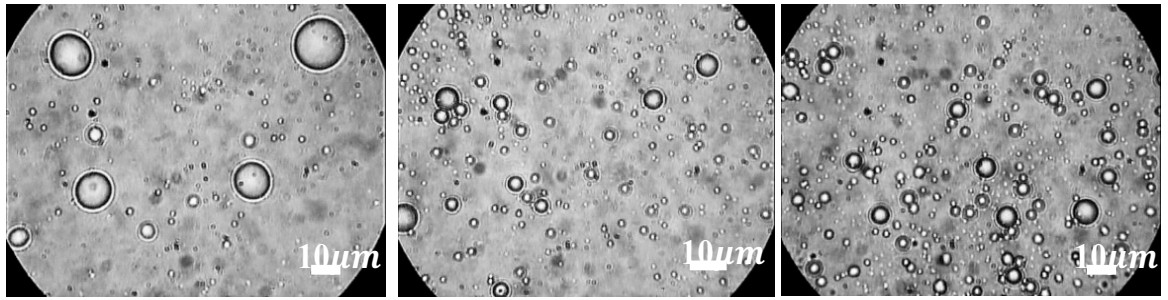
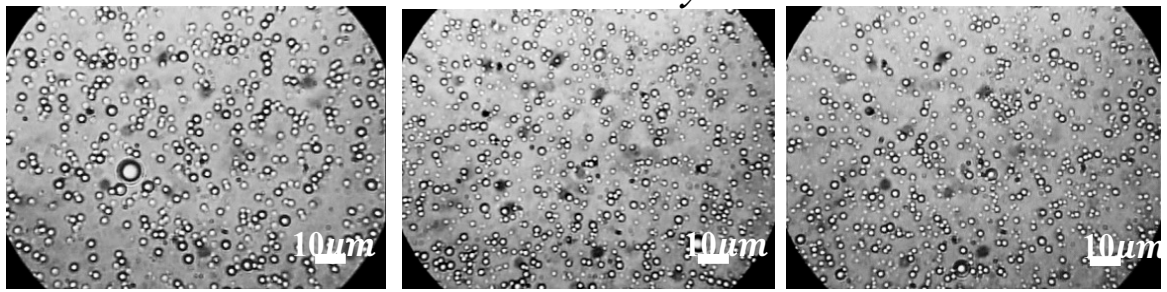
Differential Interference Contrast Microscopy with Microemulsion in a Fluidic Channel



Upper layer



Middle layer



60 W ***114 W*** ***184 W***

Similar Observations with Diesel as the Oil Phase. These results are with Dodecane

Droplet Size Decreases As Input Power Increases

How Trivial ?

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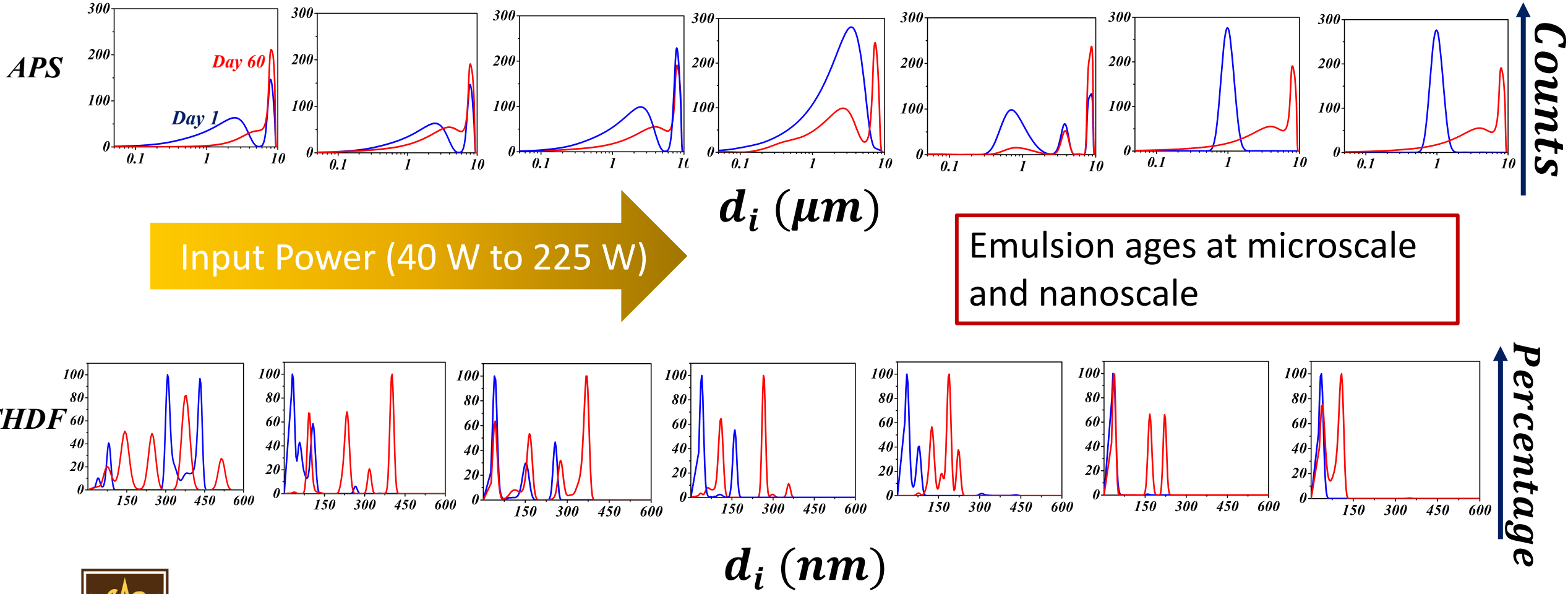
Nano sized emulsions are always formed



Emulsion ages at microscale and nanoscale

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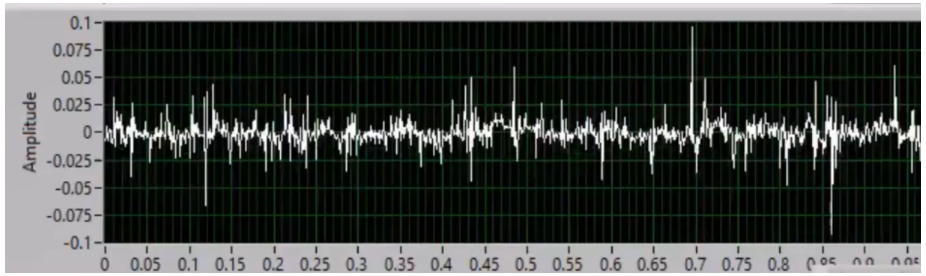
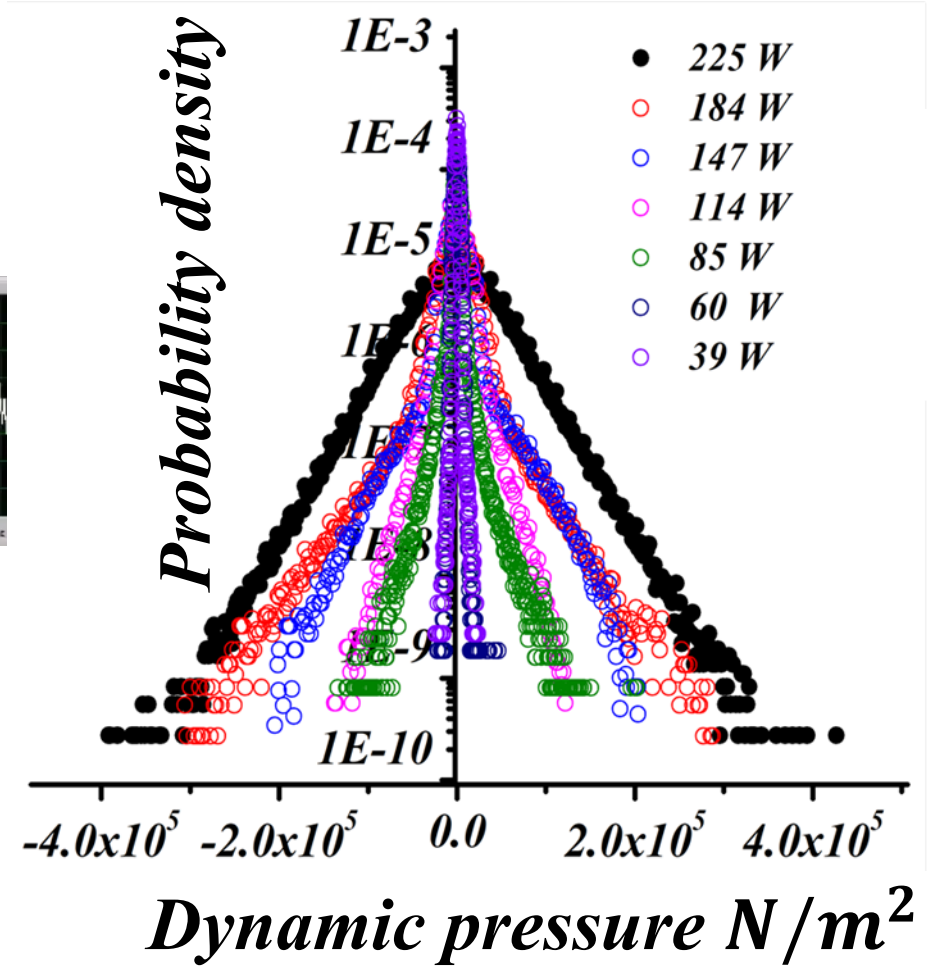
Can we correlate the particle size distribution with the fluctuations obtained from time series





$$2\gamma / R_i \sim |P_i|$$

This for distribution

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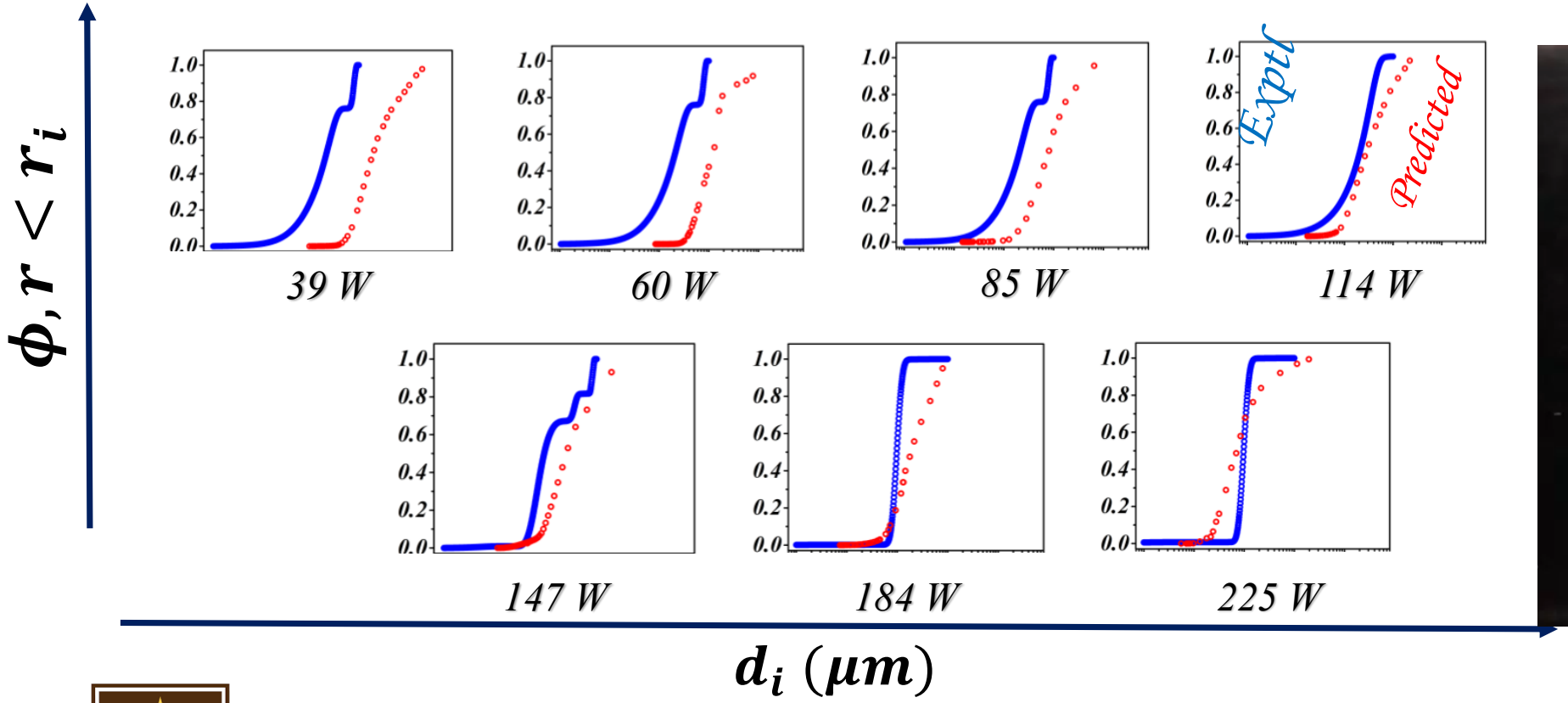
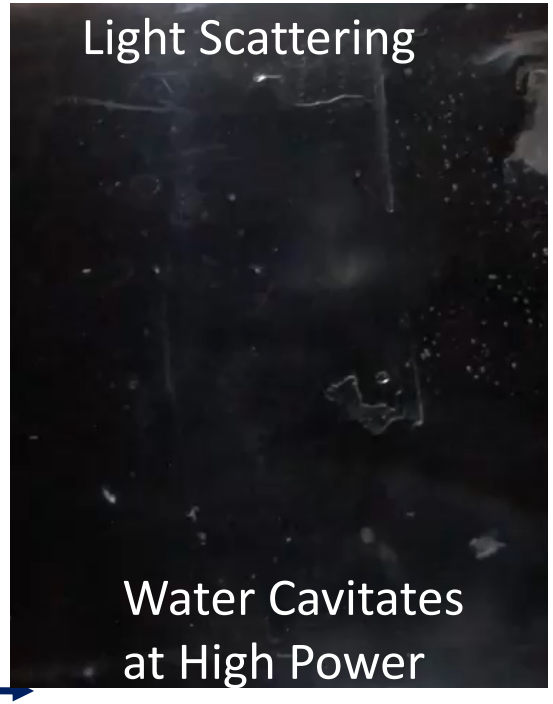
Cumulative Particle Size Distribution (APS Data)





Experimental and Predicted Trends are similar : But there are discrepancies

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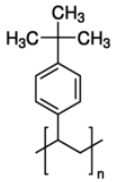
Factors Influencing Turbulence Induced Emulsification

- Air Bubbles. Generate Secondary Pressure Waves
- High MW (generally ~ 1MM) Hydrophilic Polymer (Toms Effect) suppresses Turbulence
- High MW Hydrophobic Polymer. Can Modify Rheological Properties of Oil and/or the Interface

Polydimethylsiloxane (400 K) in Alkane

Poly 4-tertiary butyl styrene (100K) in Diesel



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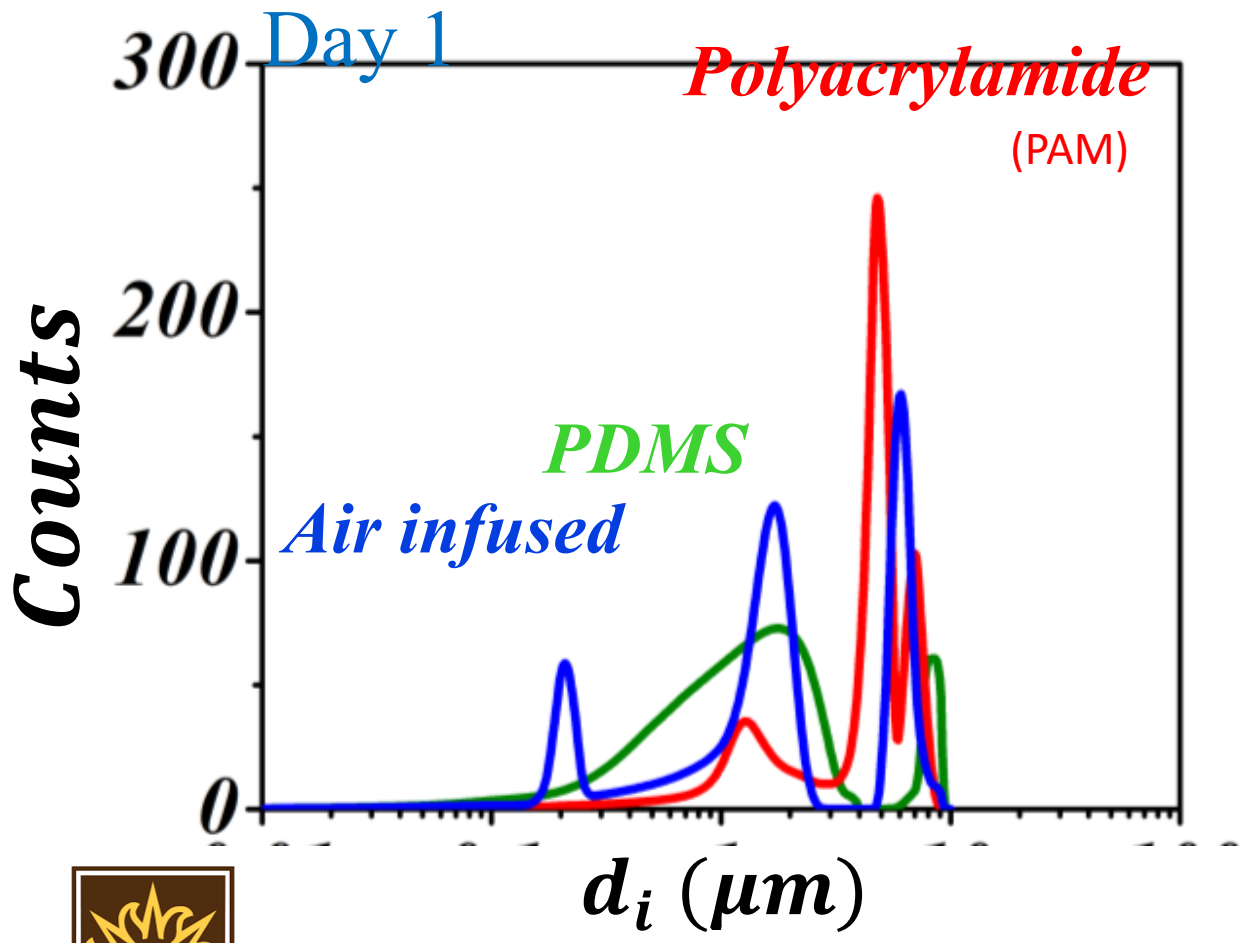
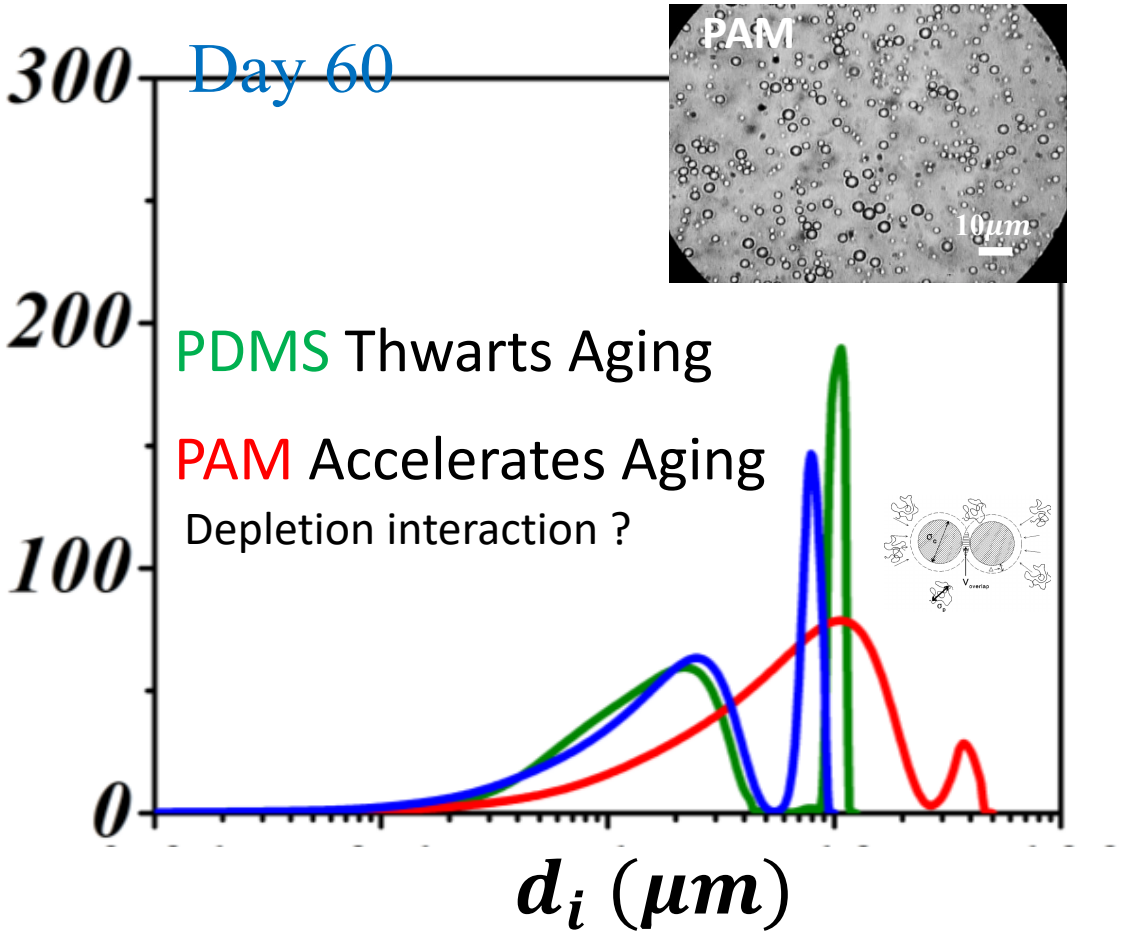
More on the Emulsification Under Different Conditions





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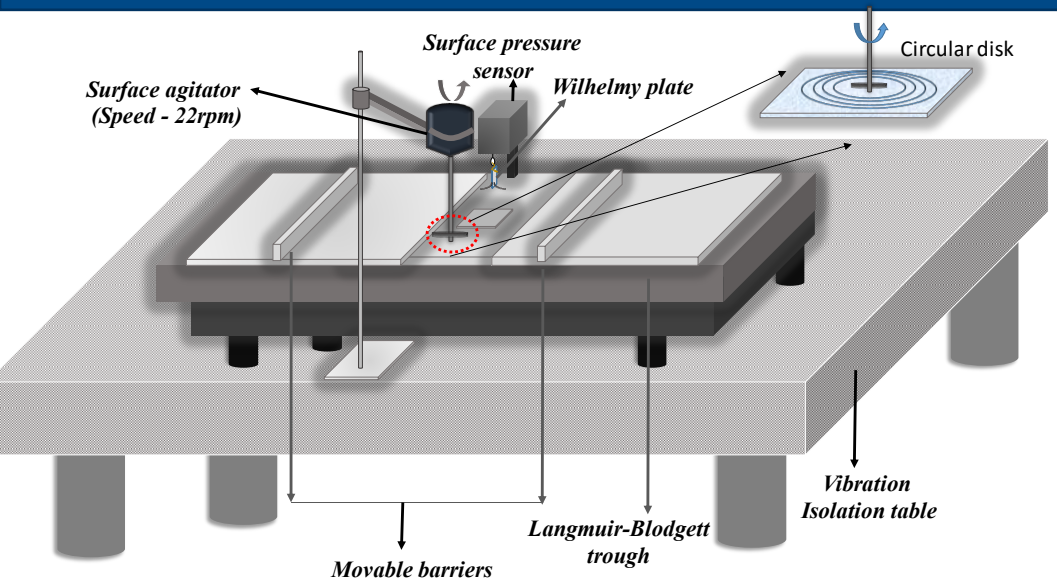
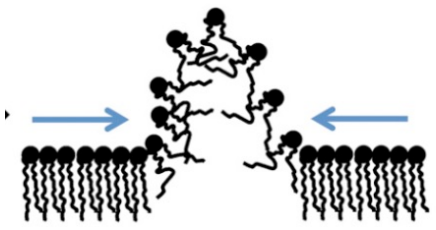
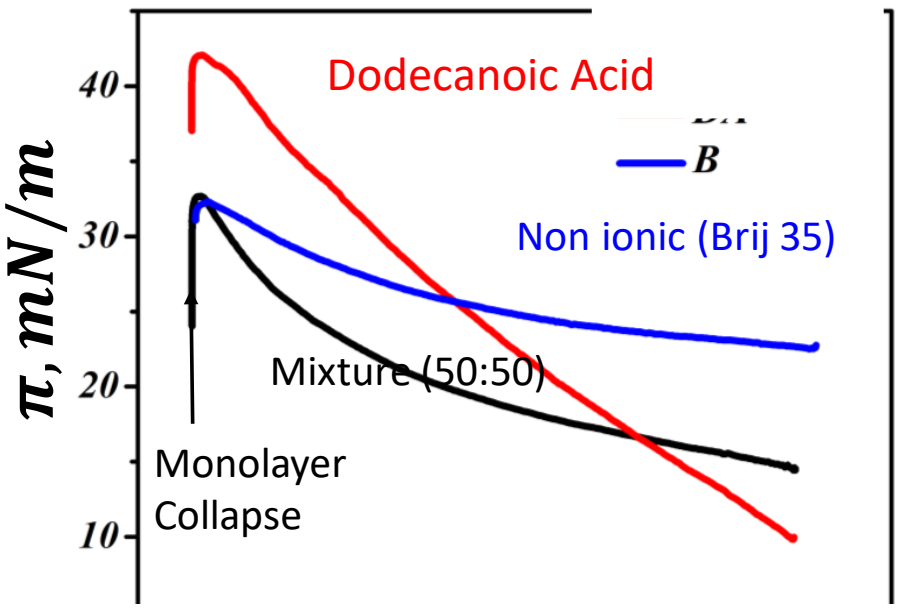
Experiments with Monolayer of Surfactant on Water
Pockels -Langmuir Balance





Folding Instability



λ ~ (Bending modulus/Surface Tension)$^{1/2}$

$A/A_{collapse}$

Quo Vadis ?

Ka Yee C. Lee, Annu. Rev. Phys. Chem. 2008

Gradzielski, Langevin, Farago, *PRE* **1996**,

Kwan and Borden, Adv. Coll. Int Sci (2012)

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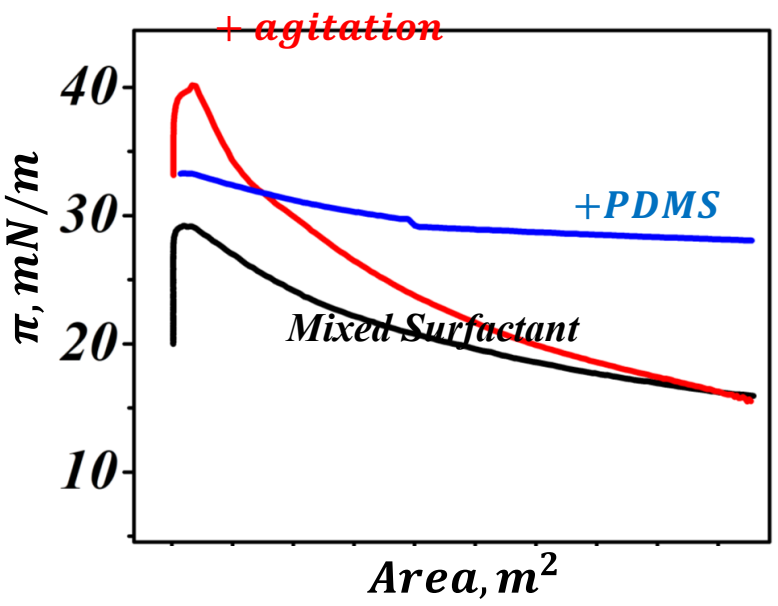
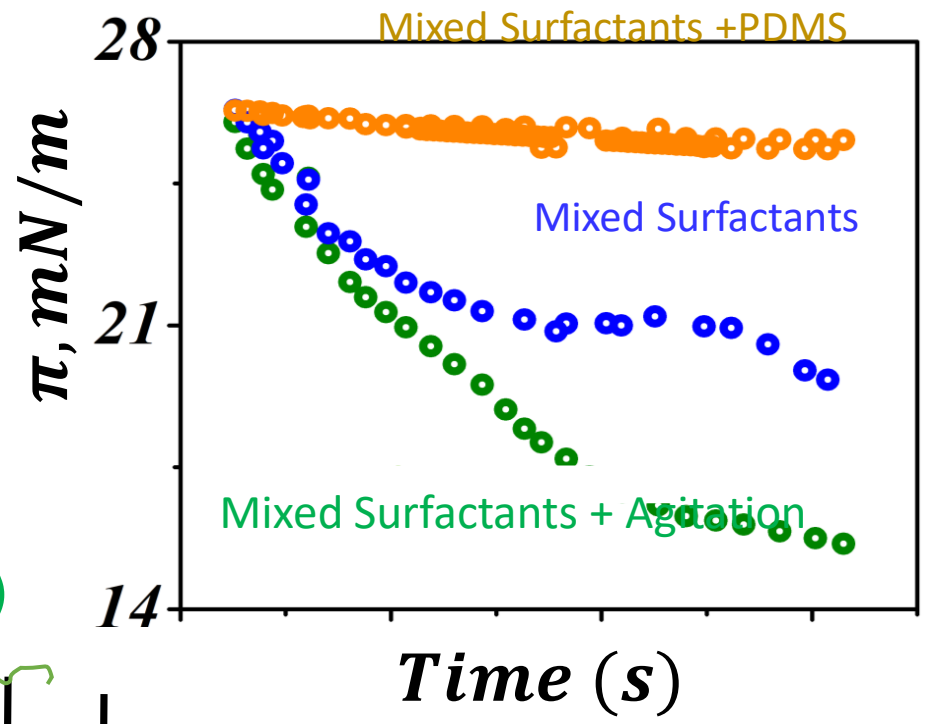
Compromised and Enhanced Stability of Monolayer



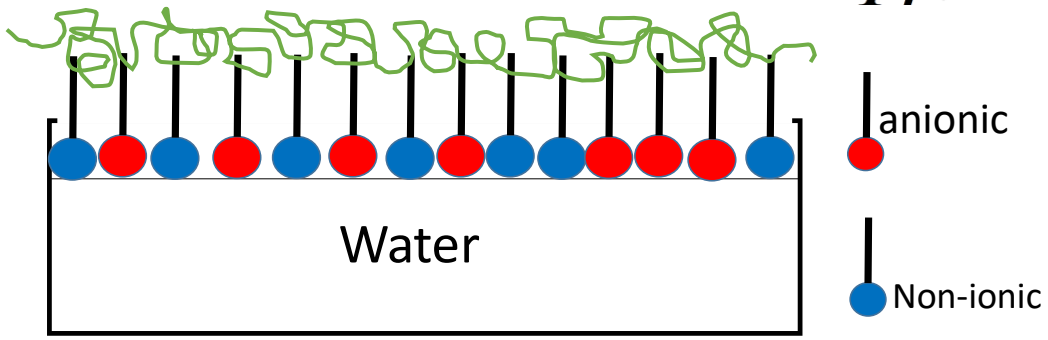
$$\frac{d\gamma}{dx} \propto -\frac{d\pi}{dA} \rightarrow 0$$

No or Little Marangoni Instability

(May be General)



PDMS (molecular rubber band)



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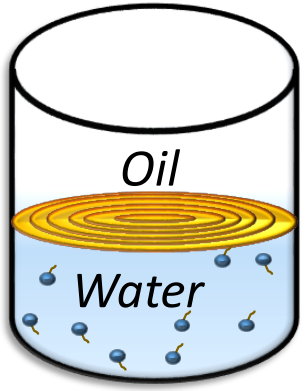
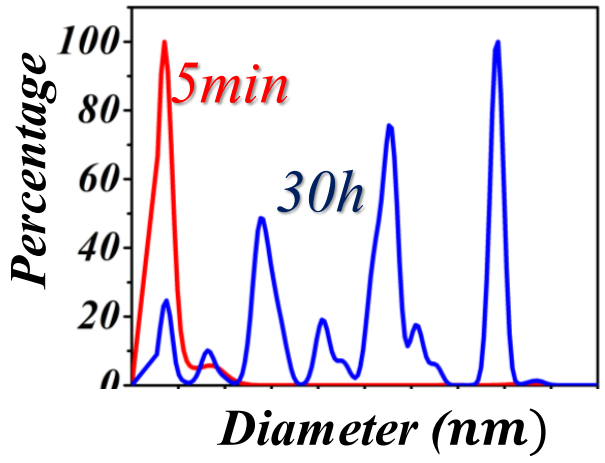
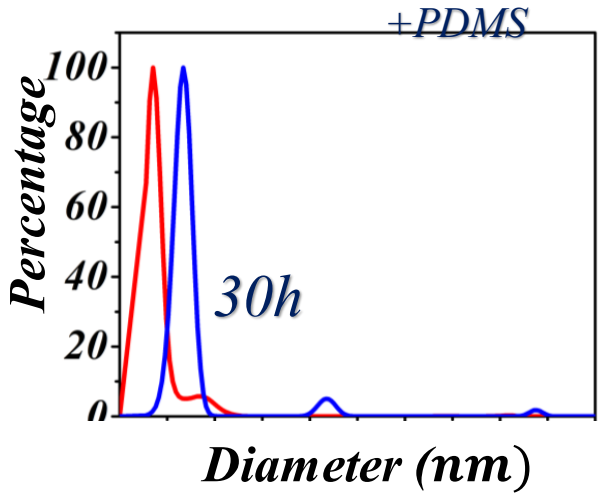
What happens when there is no external agitation ?



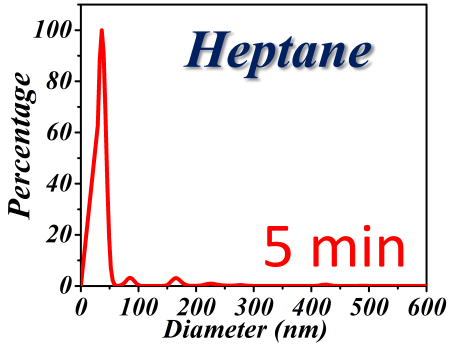


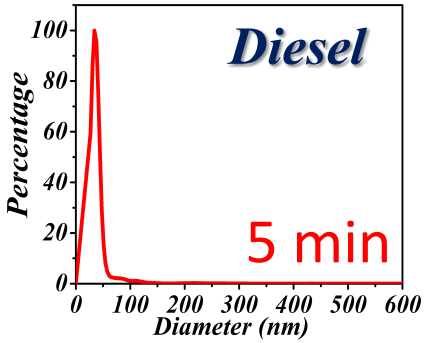


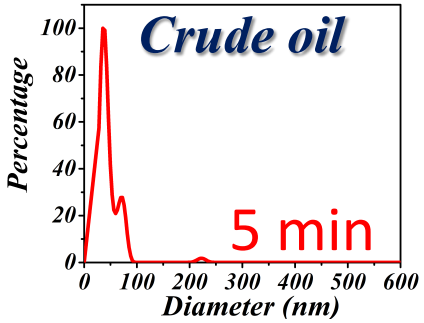
PDMS suppresses aging!

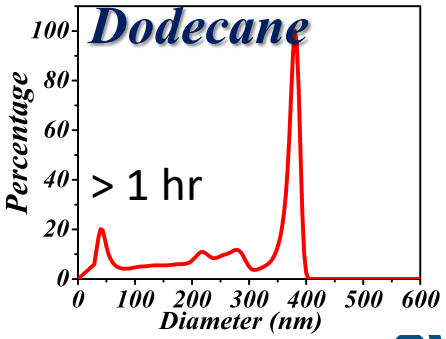
Neither Surface Tension, nor Shear Viscosity changes

Nano sized emulsions have been found to form always!

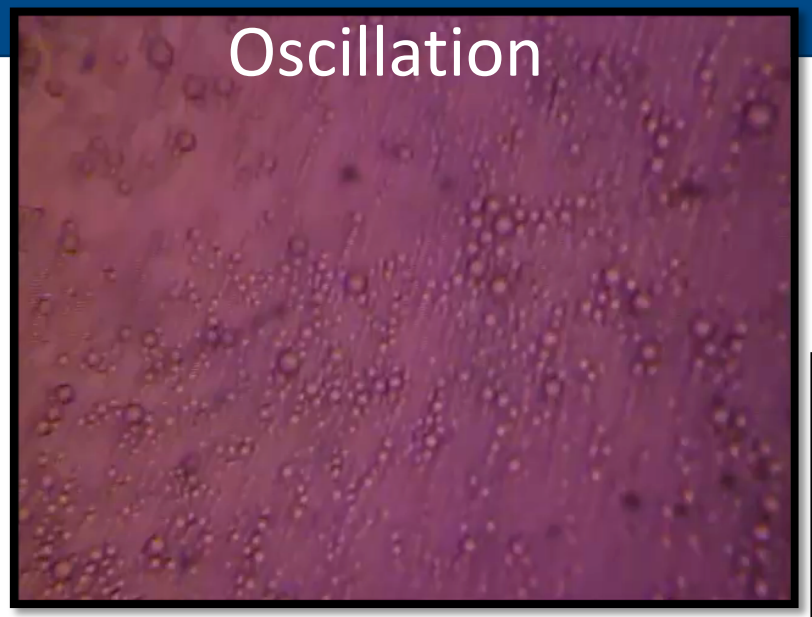


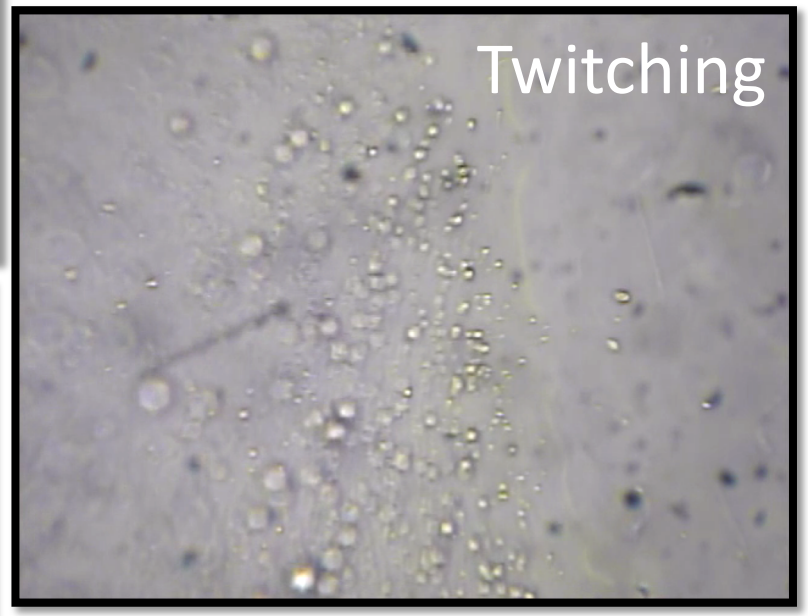


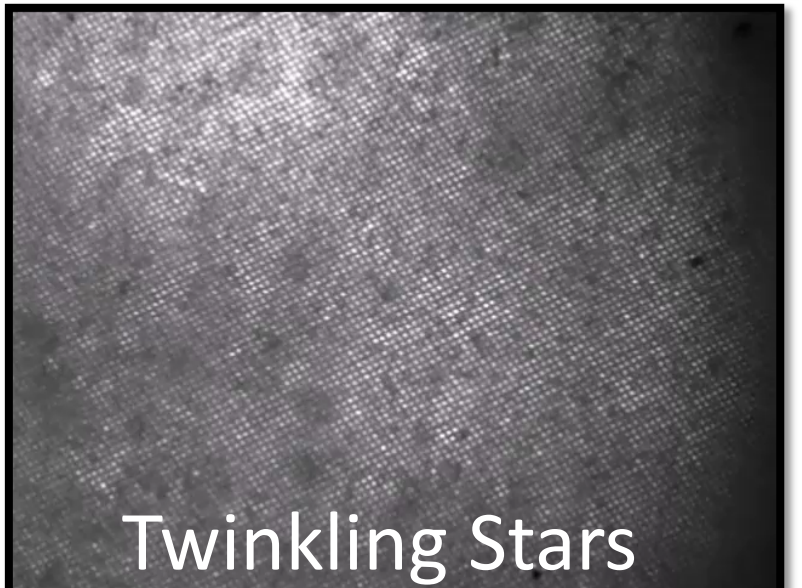




Interfacial Region is Highly Dynamic







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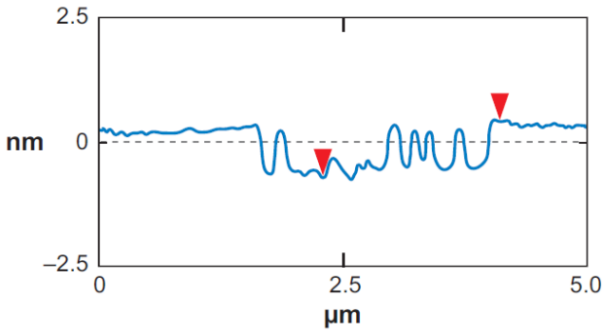
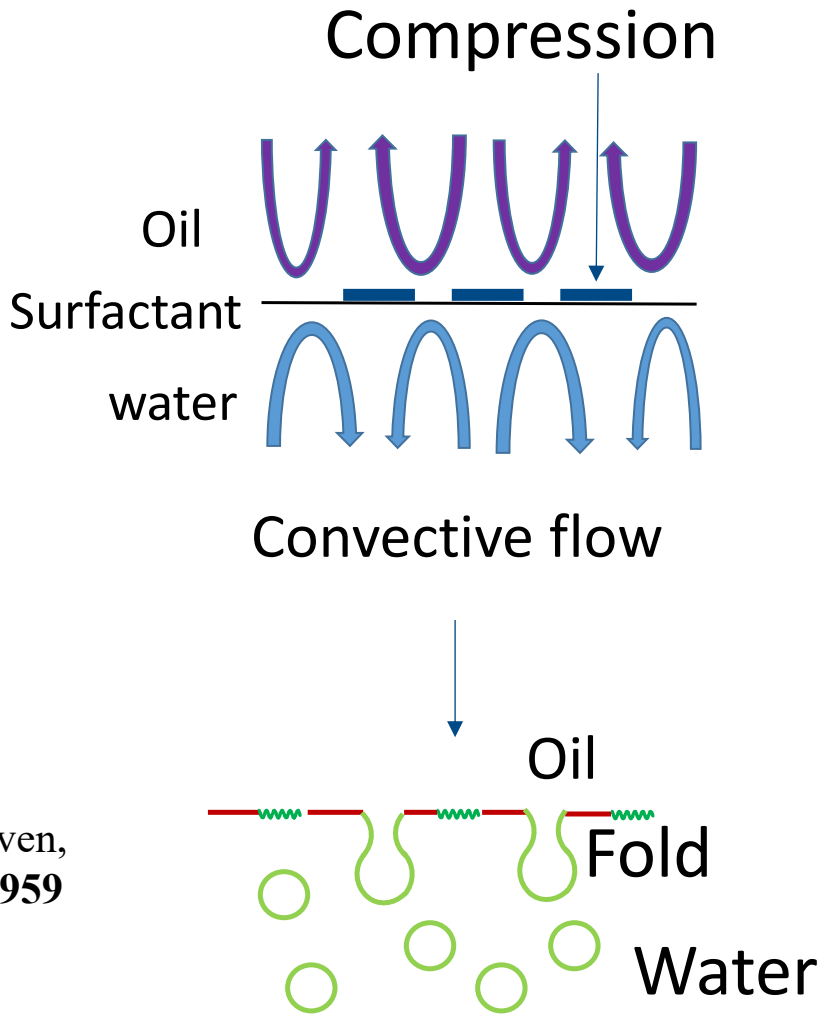
Folding Instability

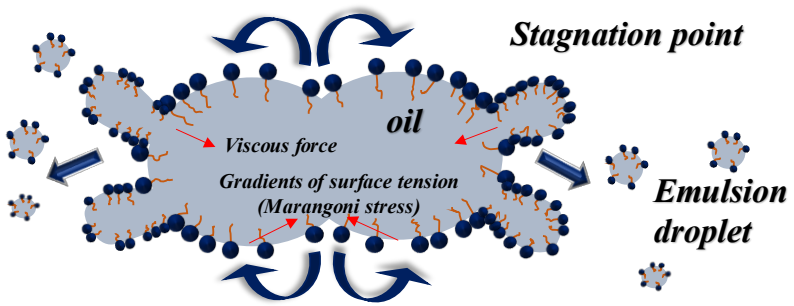


Folding Instability due to Mechanical Compression

Can this happen under fluid flow ?



Sterling and Scriven, *AIChE Journal* **1959**



Even during Turbulence Induced drop break up ?

- Marangoni Instability
- Diffusive Instability
- Landau Darrieus instability
- Role Heterogeneity (dynamic or chemical)?

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Summary

- Emulsification is a non-equilibrium process, even when there is no external agitation
- Interfacial instability and microscopic flow together lead to emulsification
- Need to go beyond the standard Kolmogorov-Hinze model to understand agitation Induced Emulsification (secondary instability)
- Interfacial tension alone is not a sufficient variable for emulsification.
- Roles of surface elasticity (Bending, Hookean and Gibbs elasticities) should also be considered

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Funding from SERDP (#WP18-1074) is Gratefully Acknowledged

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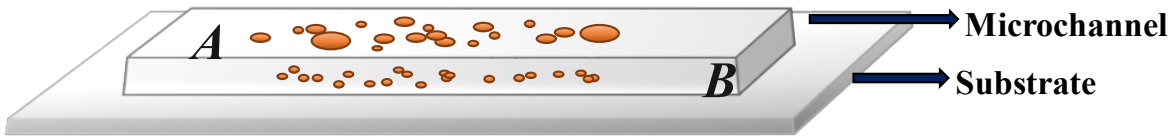
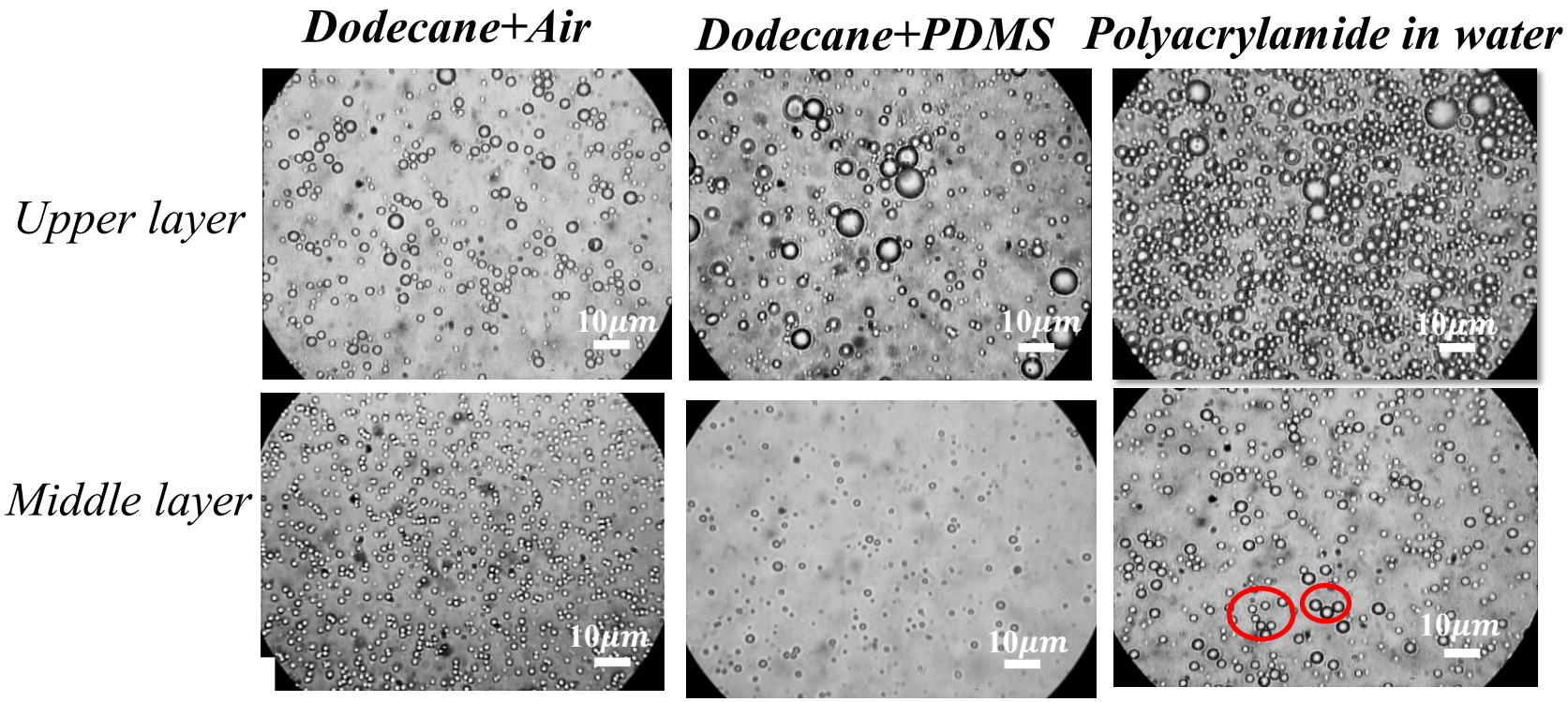
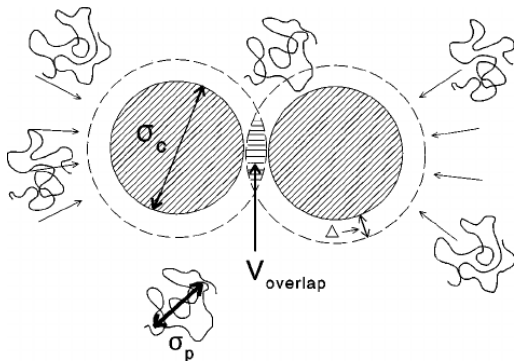
Extra Slides

Not for Presentation

Emulsification Under Different Conditions







Depletion interaction ?

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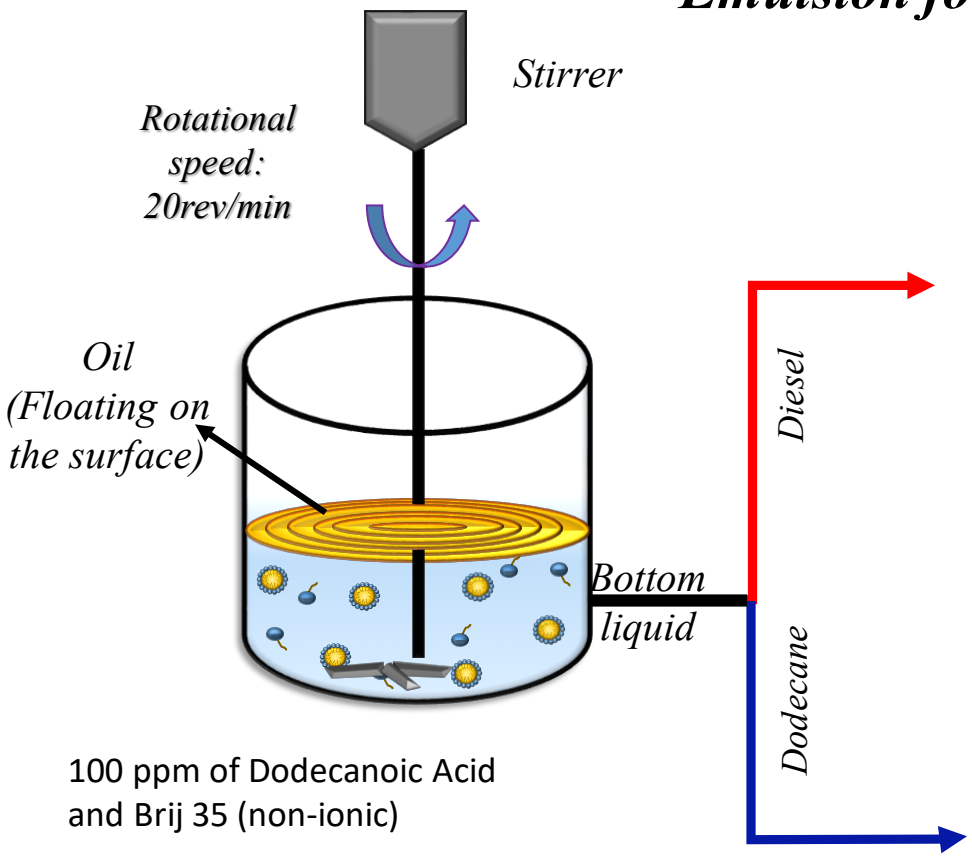
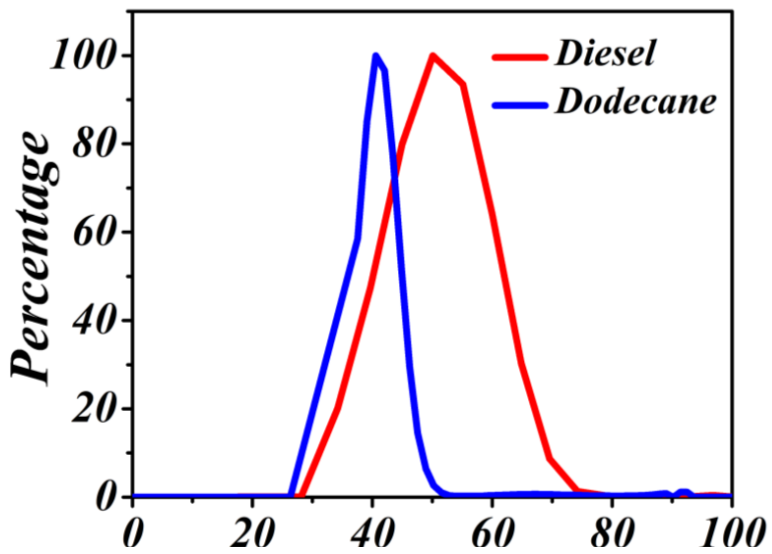
Emulsion formation – very slow stirring



Capillary Hydrodynamic fractionation



100 ppm of Dodecanoic Acid and Brij 35 (non-ionic)

1000 ppm oil

0.6 M Salt Water

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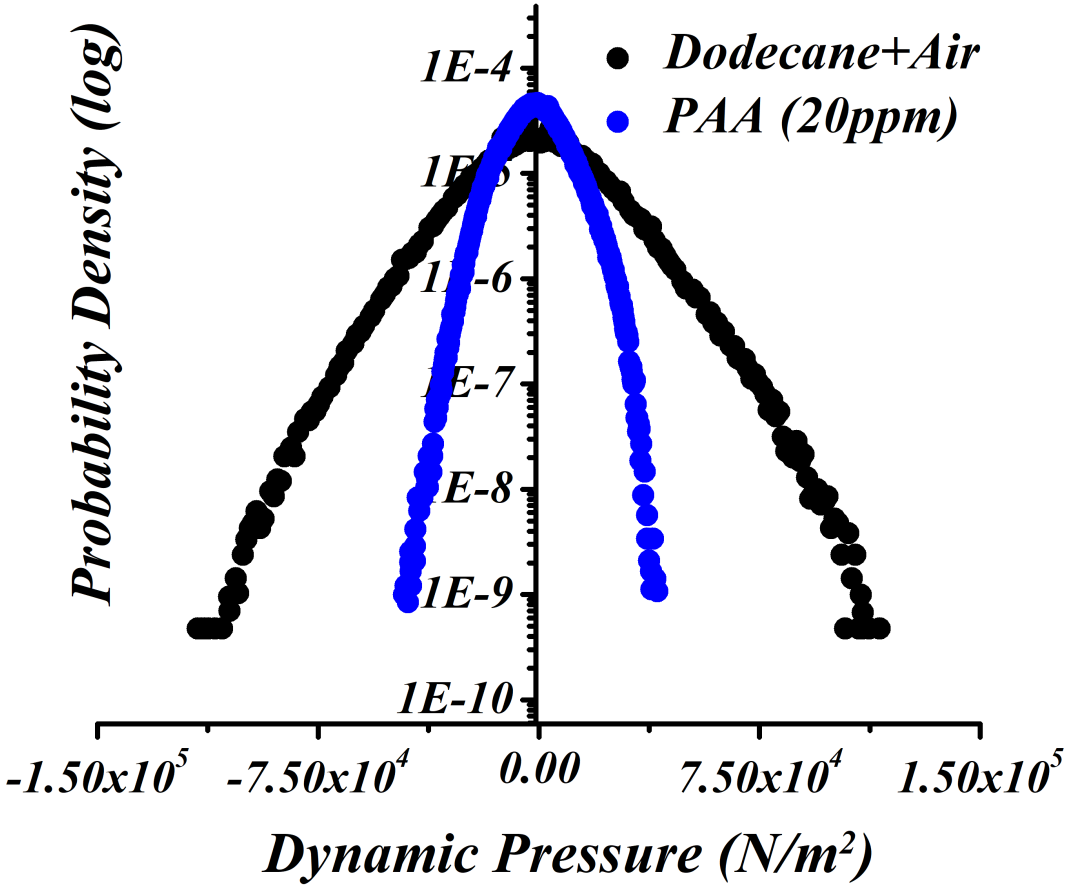

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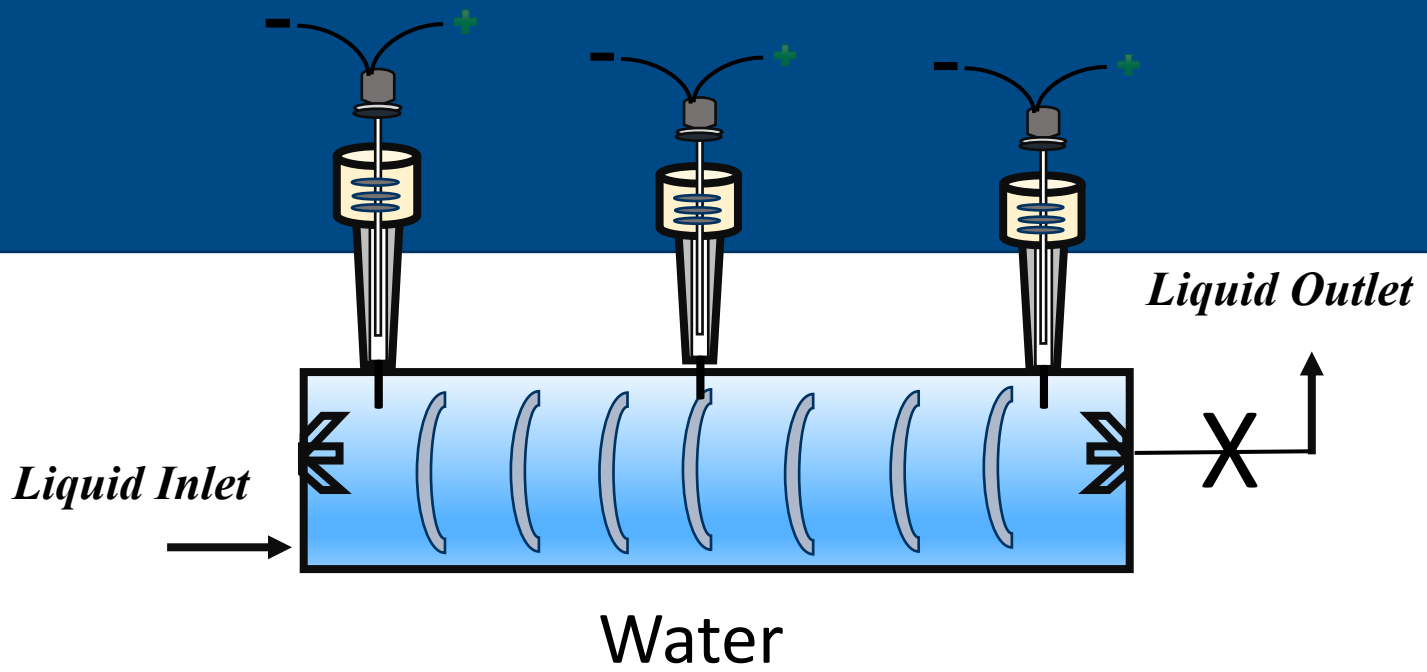
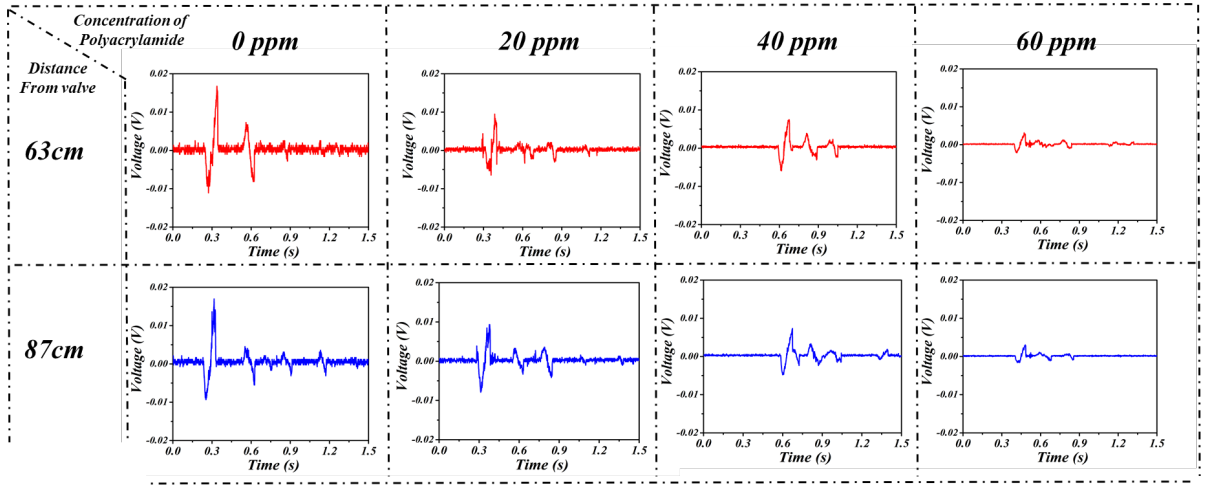


Pressure Wave

Why study this ?

The scattering of pressure waves is important in Turbulence and emulsification



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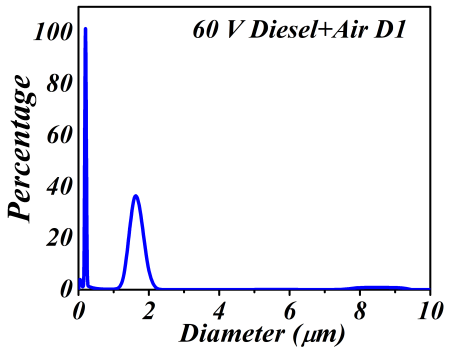
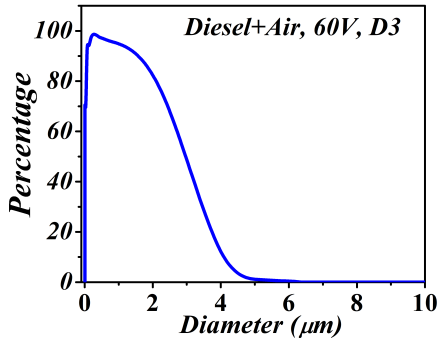
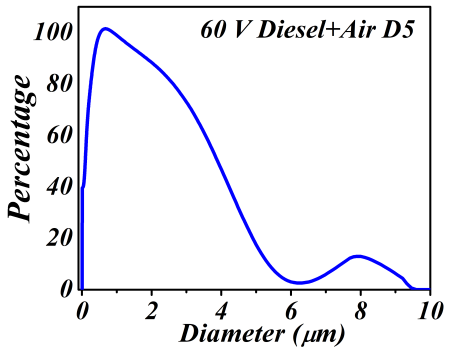
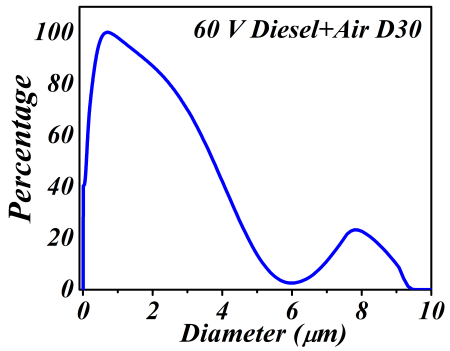
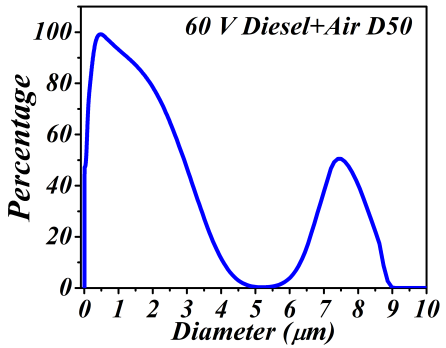
Diesel



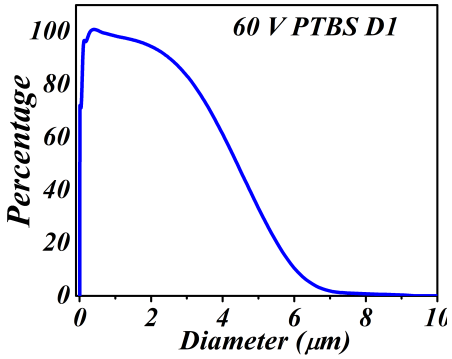


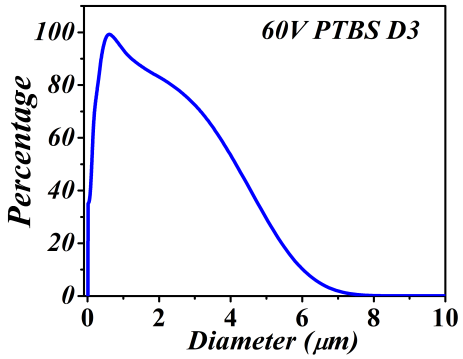


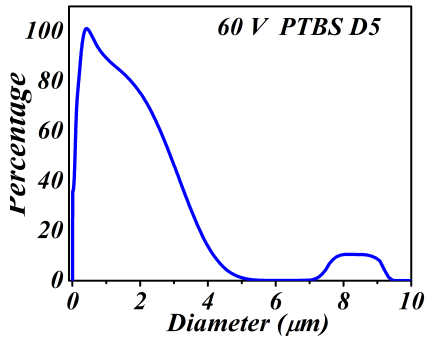


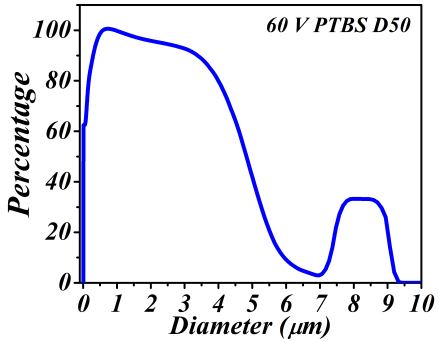


Air









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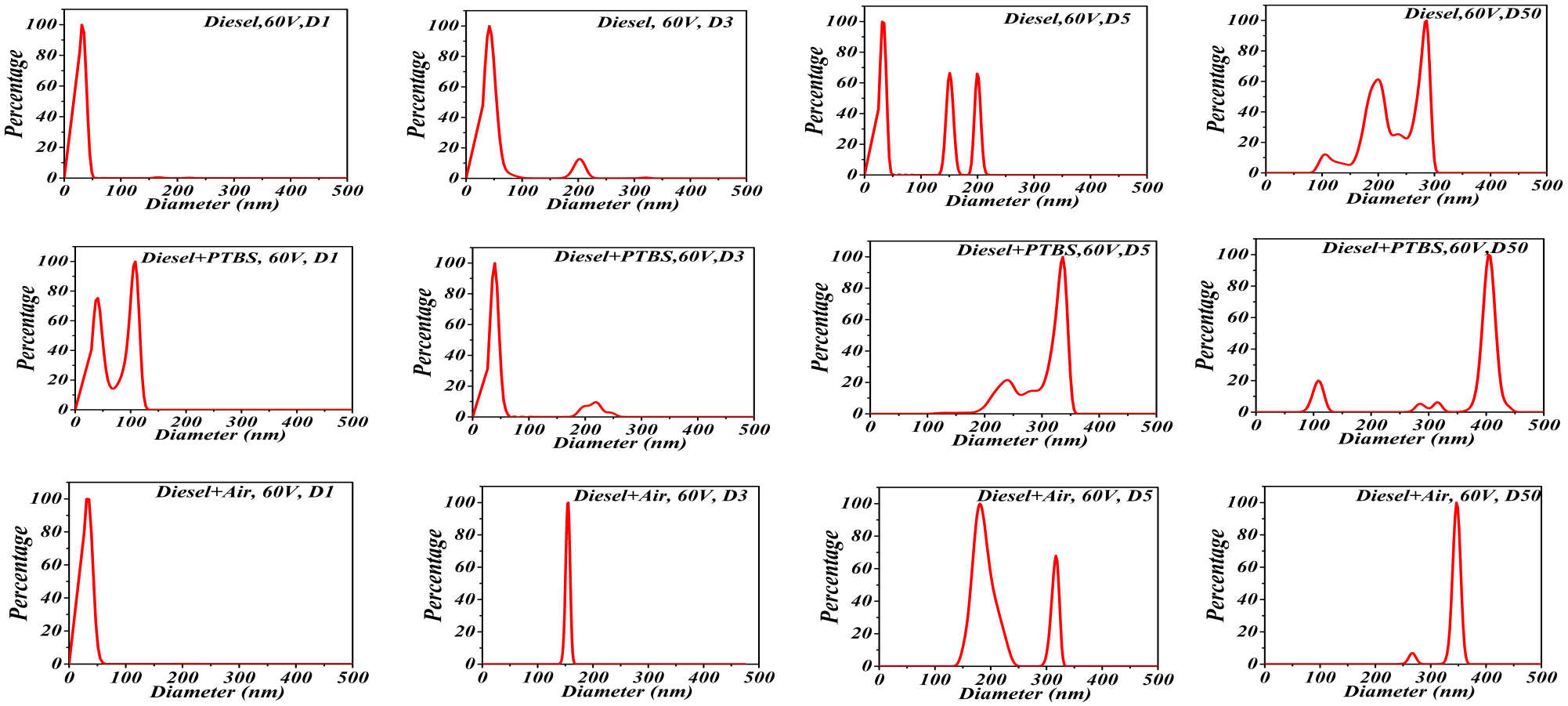

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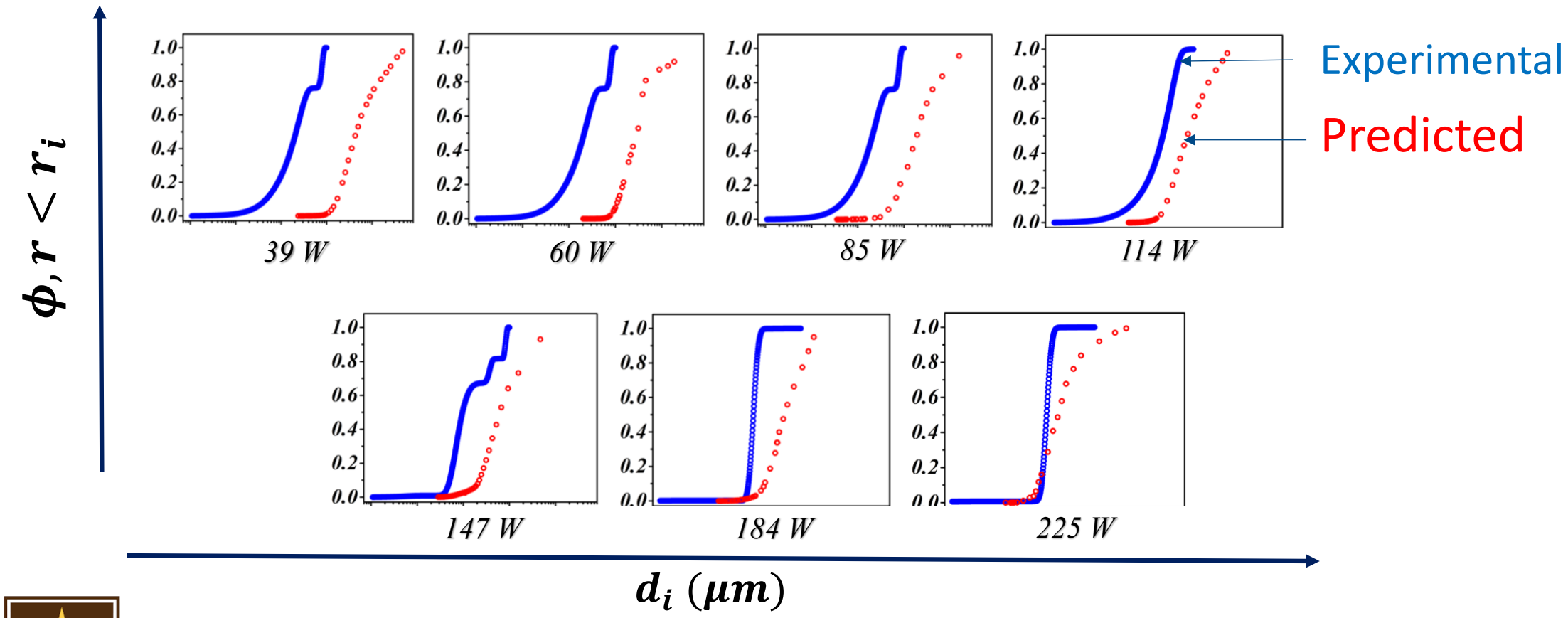
Cumulative Particle Size Distribution (APS Data)



Experimental and Predicted Trends are Similar :
But there are discrepancies quantitatively

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