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Macro- and Micro-Scale Flow in Oil-Water Emulsions

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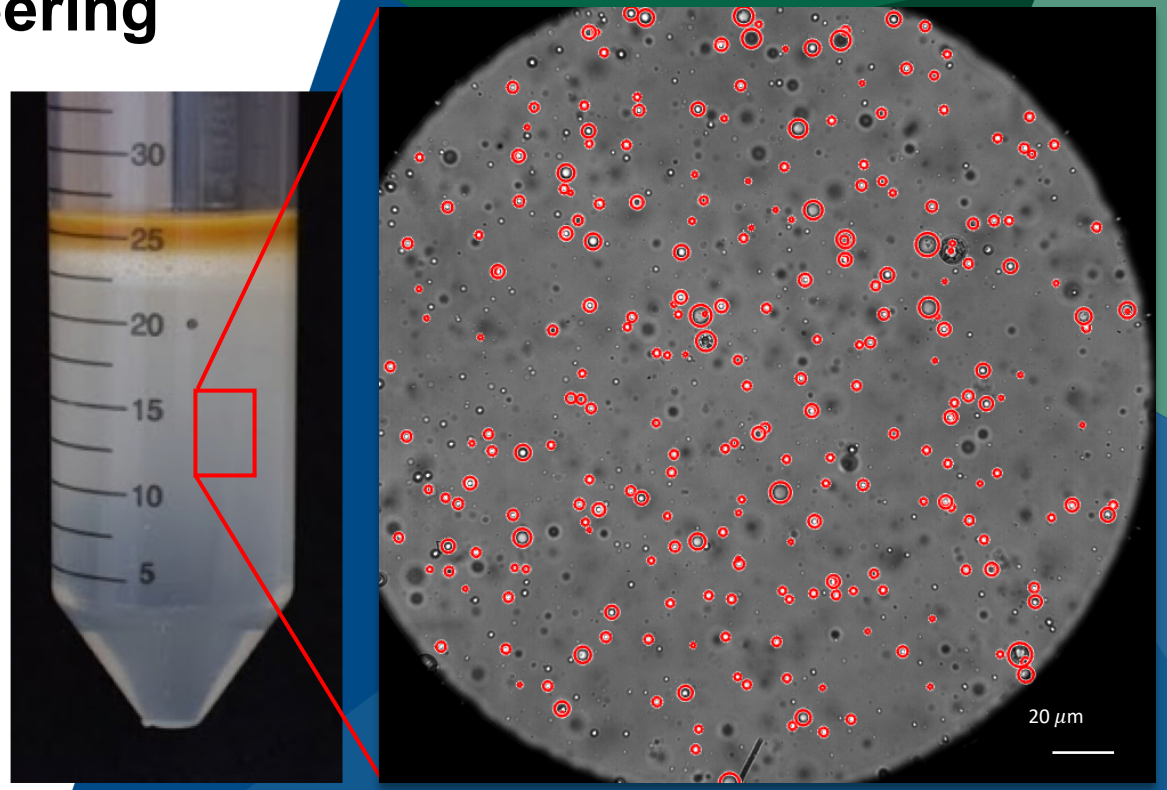

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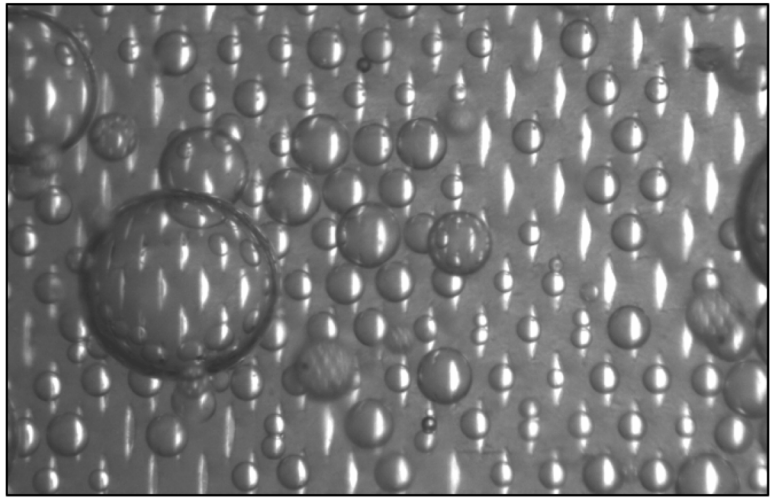
Liquid – liquid emulsions: Often undesirable

Fuel-water separators



Brad Hauser (Donaldson)

Example of rust, pitting, and wear on Injectors

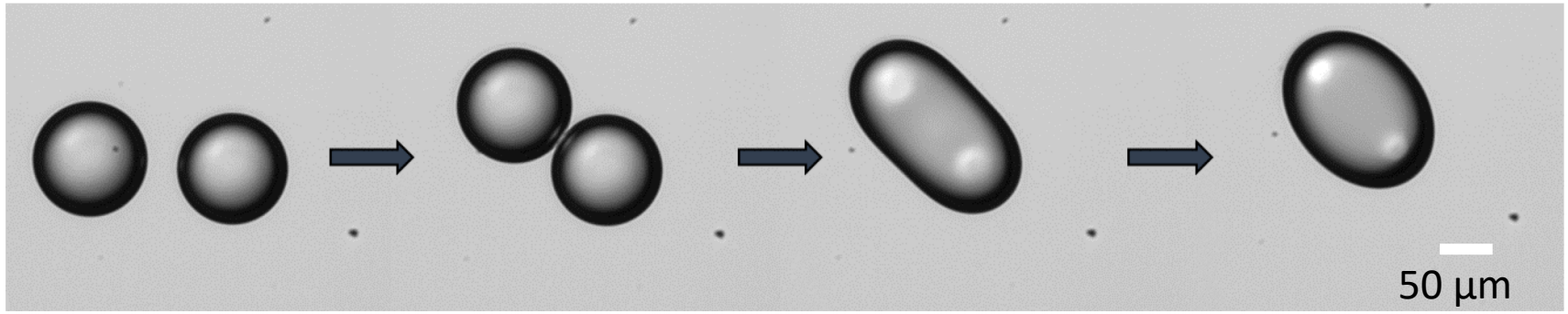
Shipboard emulsions

(water drops in fuel) Water droplets in diesel fuel lines cause rust, abrasion, spalling, icing and microbial growth

(oil drops in water) Water with > 15 ppm of oil, such as bilgewater, cannot be discharged overboard

Liquid – liquid emulsion treatment

Coalescence is often a necessary ***treatment process*** to separate drops from a liquid



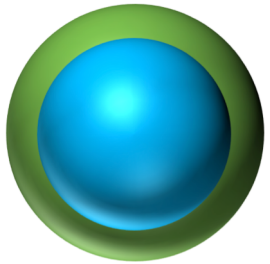
- **Primary treatment** for large drops (> 30 μm).
  - Drops relatively **easy to separate.**
  - Big enough to readily settle by gravity (settling tanks) or wet surfaces (coalescence plates).
- **Secondary treatment** for small drops (< 30 μm).
  - Much more **difficult to separate.**
  - Drops too small to settle without aid (membranes).

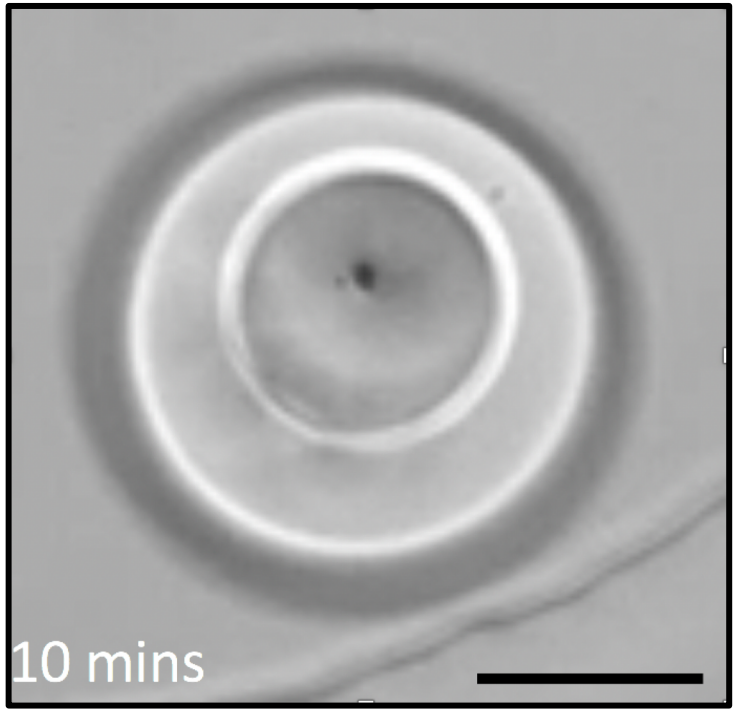
http://www.marineinsight.com

Challenge: Chemically stabilized emulsions

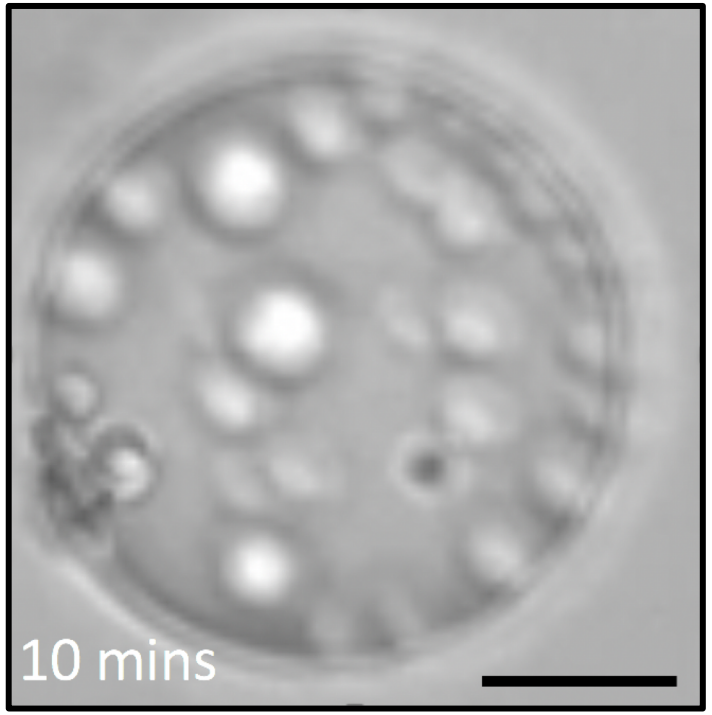
Surfactants lower the thermodynamic driving force for coalescence

Higher IFT, Readily phase separates



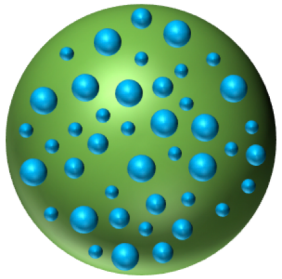


Less surfactant



More surfactant

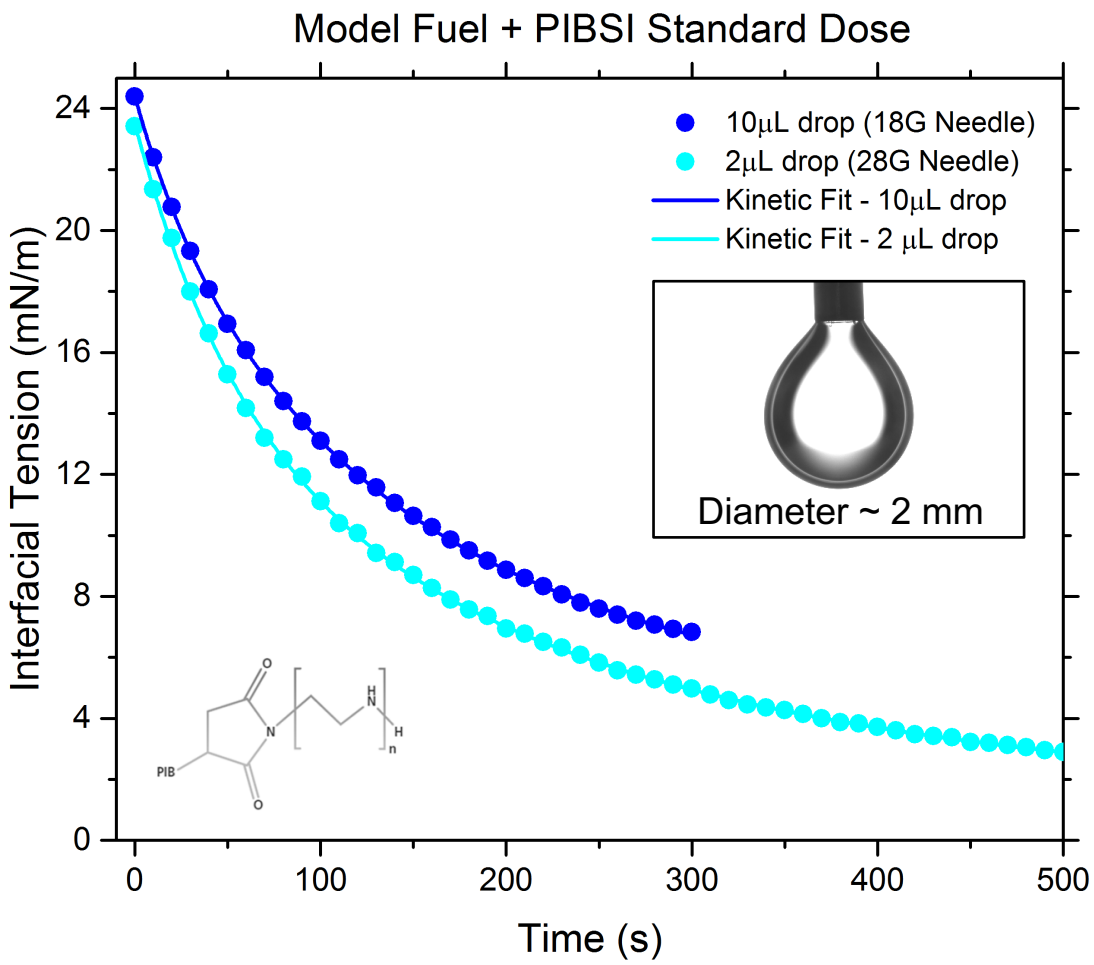
Lower IFT, Remains emulsion

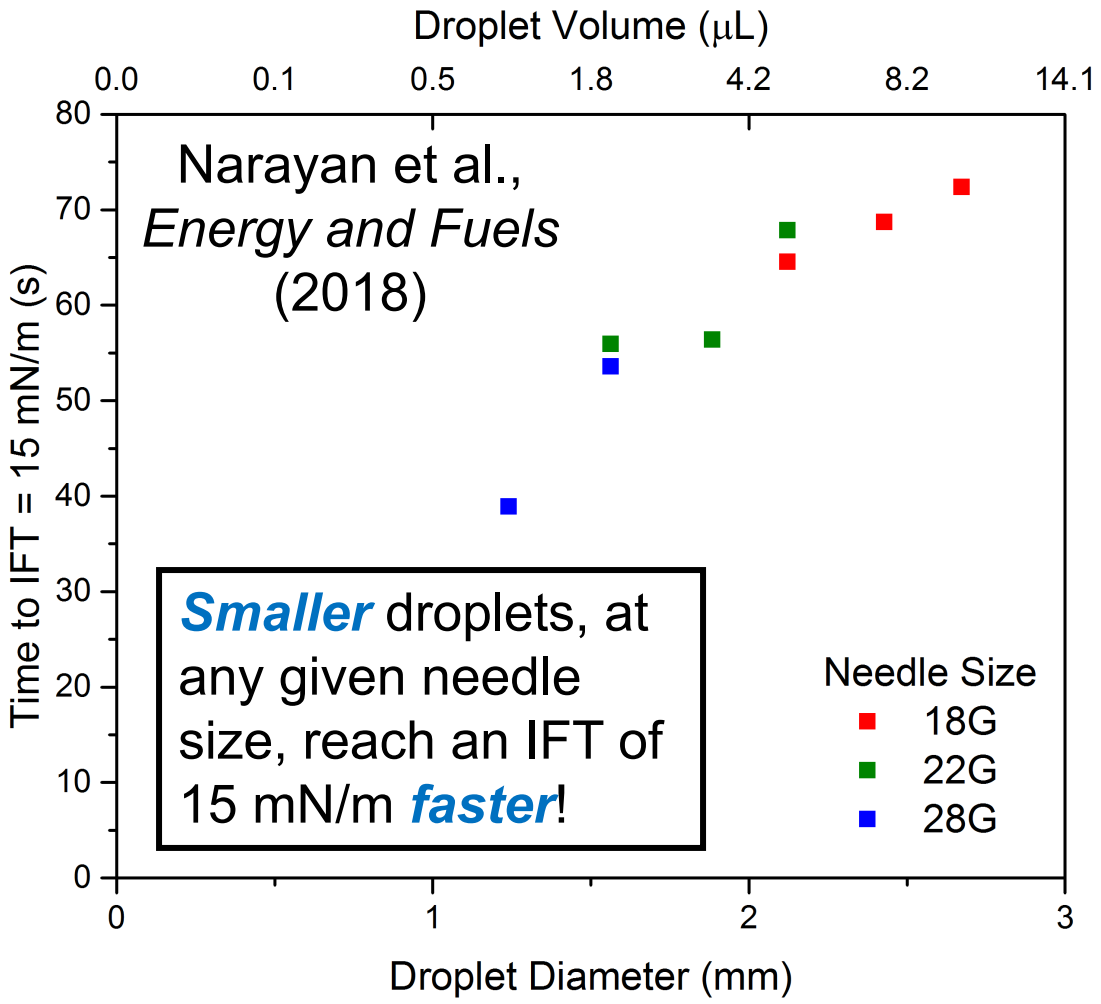


Surface active additives ***inhibits coalescence*** and ***lowers filtration performance.***

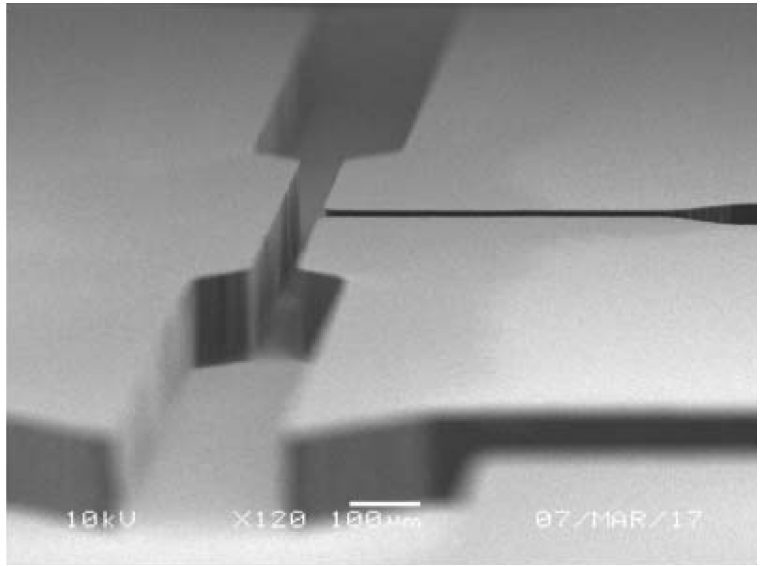
Nandy and Dutcher, *JPC B* (2018) – Scale bar is 50 μm

Challenge: Properties are size dependent

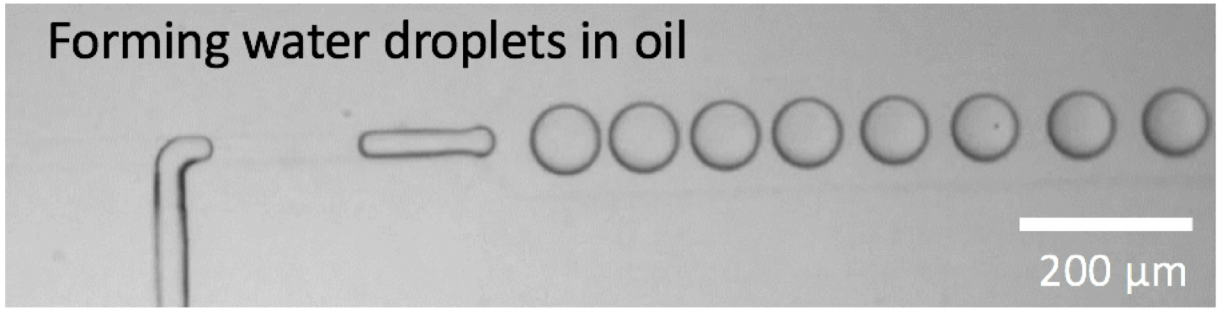




Solution: Microfluidics for microscale drops

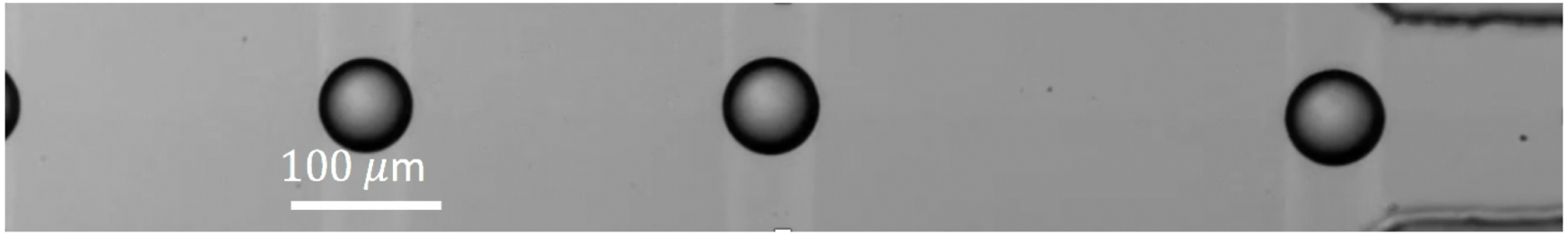


SEM image of a microfluidic device
Metcalf, Narayan & Dutcher, *AS&T* (2018)



We use microfluidic platforms to measure interfacial properties at ***relevant length and time scales***.

Force balance on deforming droplet

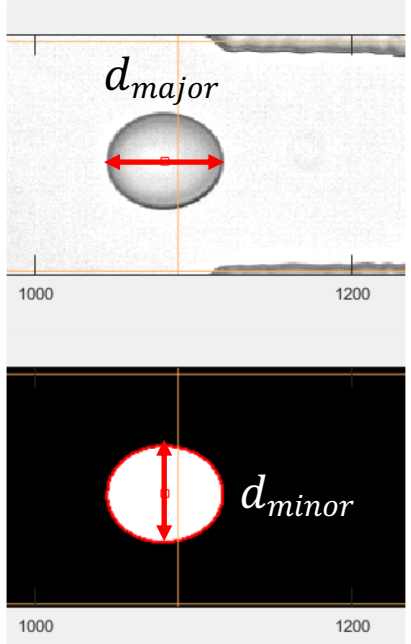


Frame rate: 32,000 fps

Shape deformation can be used to measure interfacial tension

Deforming force from the flow	Material change in deformation	Restoring force due to interfacial tension

$$\alpha\eta_c\left(\frac{5}{2\hat{\eta}+3}\dot{\varepsilon}(x)-u(x)\frac{\partial D(x)}{\partial x}\right)=\gamma\frac{D(x)}{a_0}$$



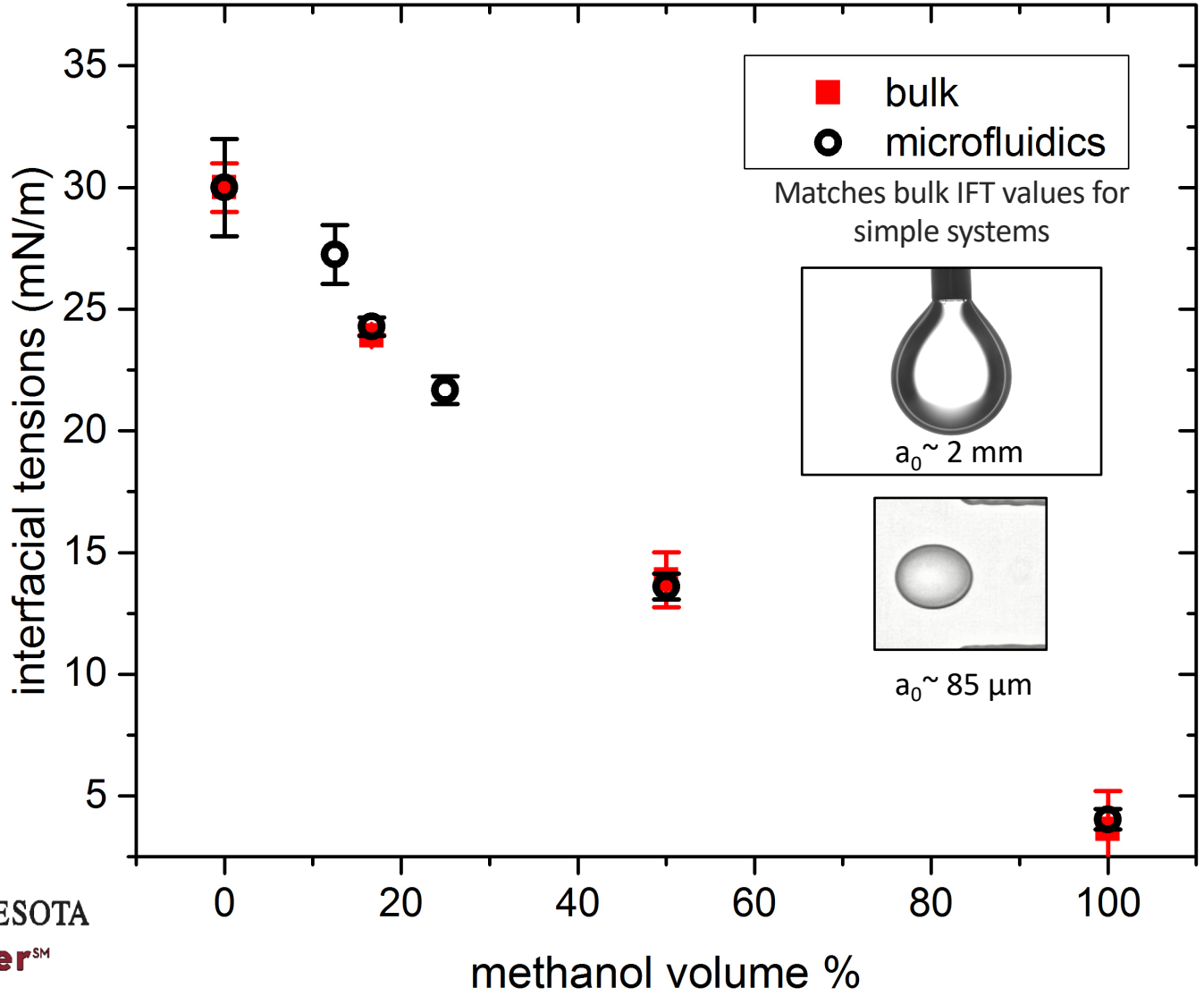
Deformed droplet

$$D=\frac{d_{major}-d_{minor}}{d_{major}+d_{minor}}$$

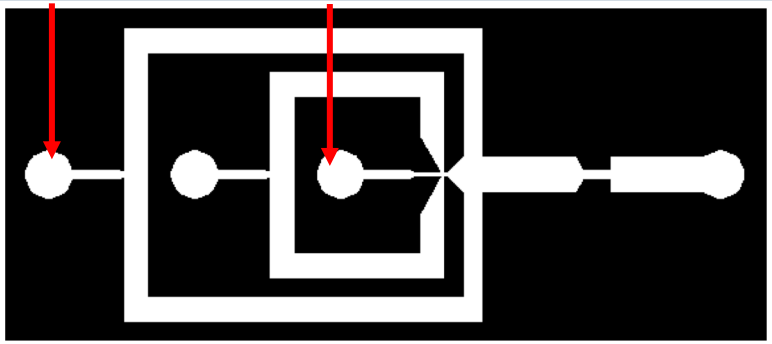
Un-deformed droplet:
Radius = a_0

Simple system: Methanol and water

Accurate measurements of IFT with small sample volumes



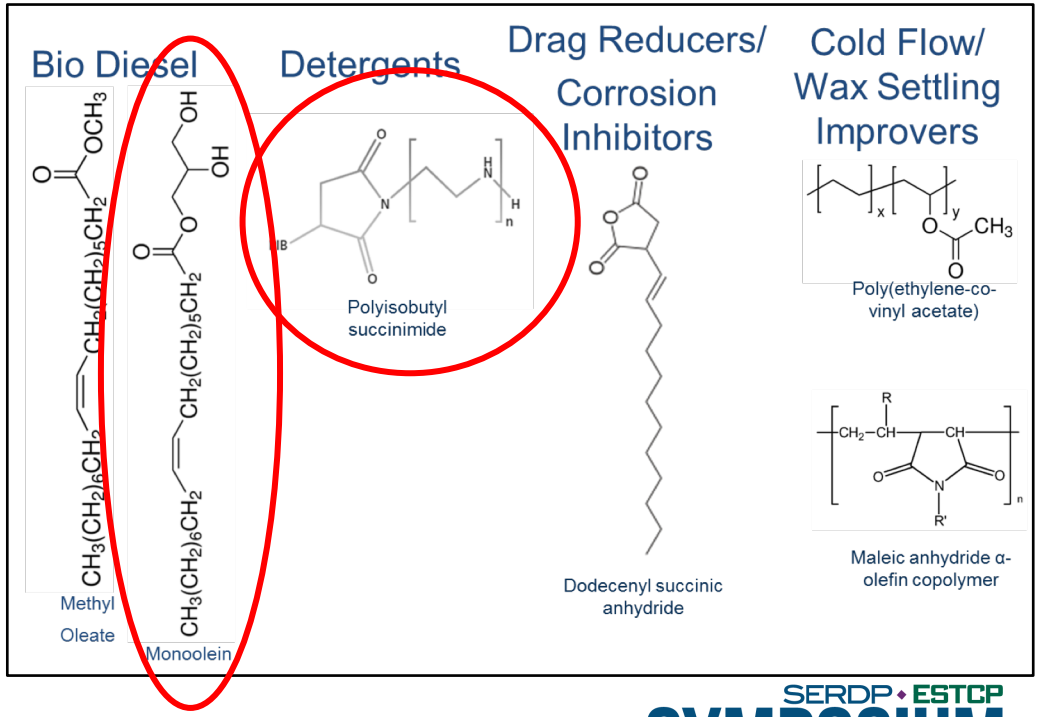
Fuel and fuel surrogate systems



Model Fuel:
Methyl-Laurate 1 – Decene

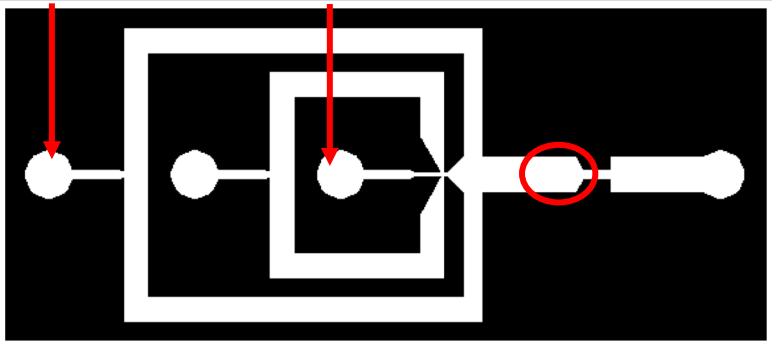
Sample	Additive	Macro IFT (mN/m)	Micro IFT (mN/m)
Model fuel	-	25.5	26.5
Model fuel	PIBSI Std. dose	dynamic	dynamic
Clay-treated ULSD	-	43.0	45.5
Clay-treated ULSD	Monoolein 0.01 mg/mL	43.0	45.5
Chevron Diesel Emission ULSD	Mixture	dynamic	dynamic

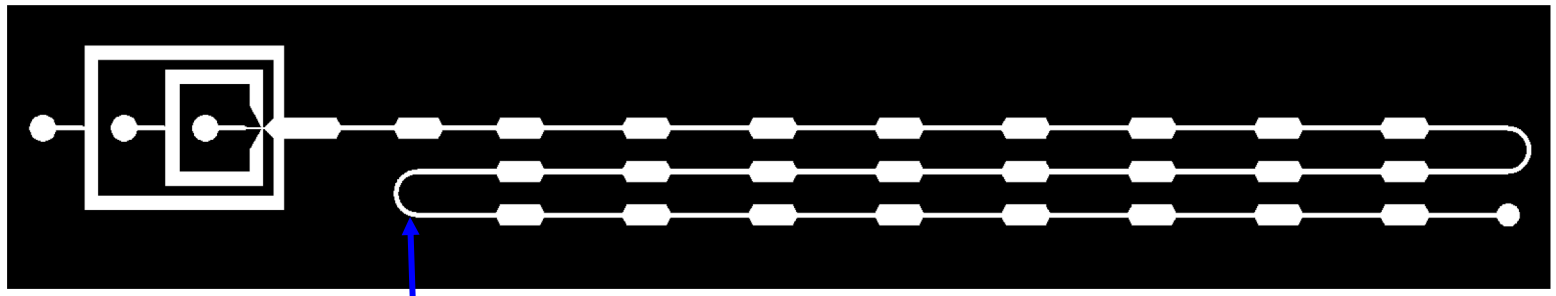
Fuels contain surfactant additives, yielding a time-dependent interfacial tension



Good agreement for static IFT (yellow arrows)

Dynamic interfacial tension measurements

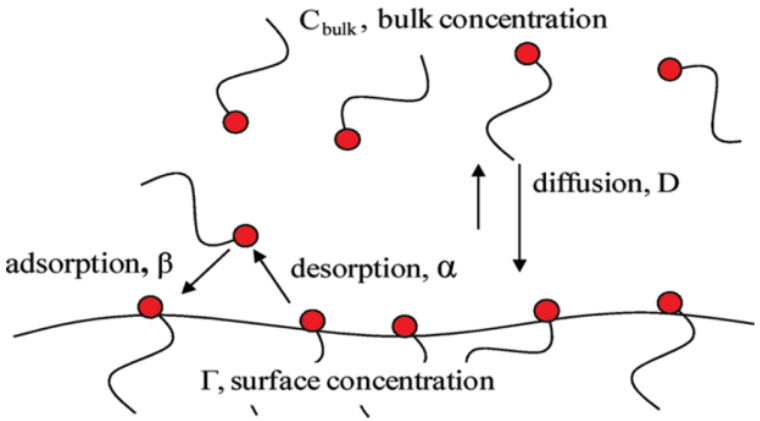




Serpentine channels for greater residence time **(~9 seconds)**

- **Diffusional** mass flux **faster to curved interfaces.**
- **Advection enhances rate of diffusion**, leads to prominent kinetically controlled dynamics.

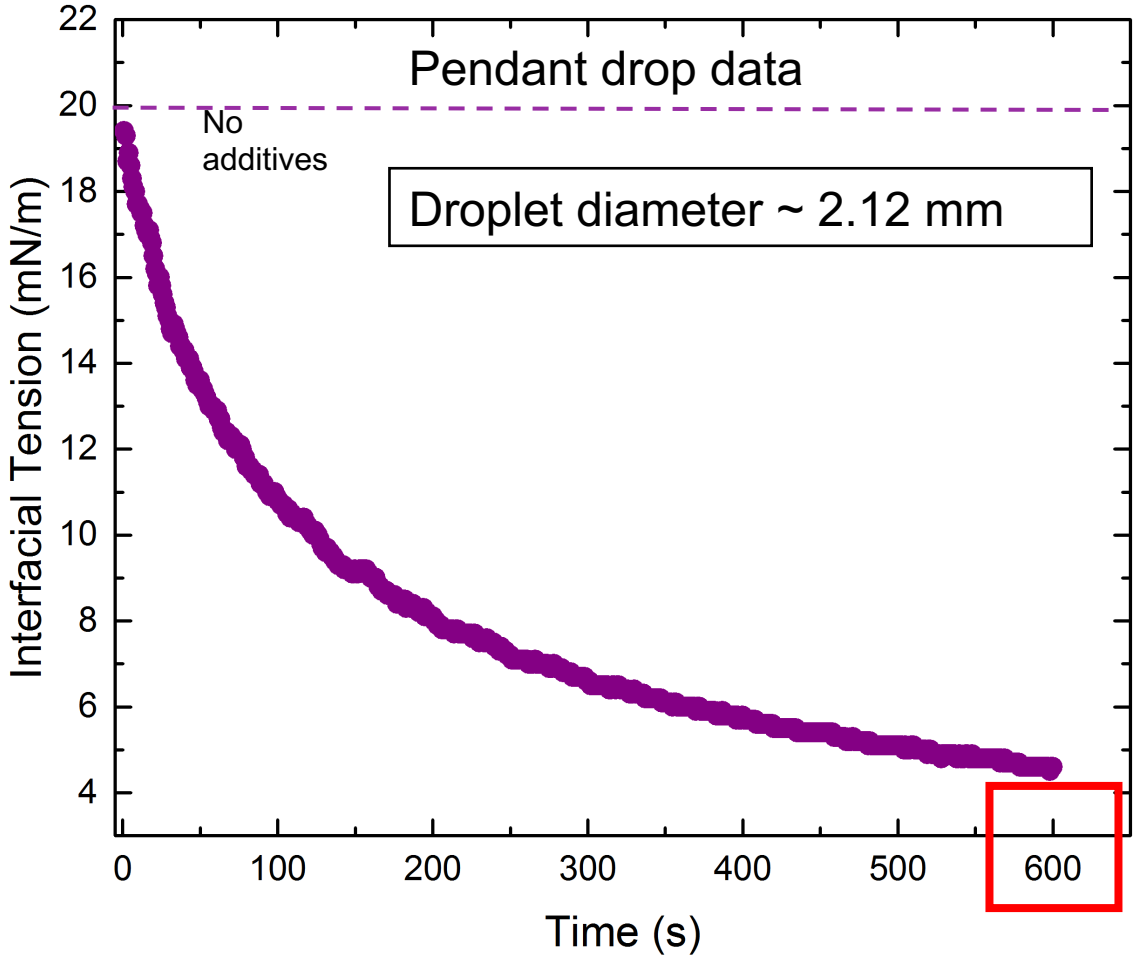
- Key references: Martin & Hudson *New J Physics* (2009); Brosseau et al., *Soft Matter* (2014), Lee et al. *Lab Chip* (2017); Narayan et al. *Energy Fuels* (2018)

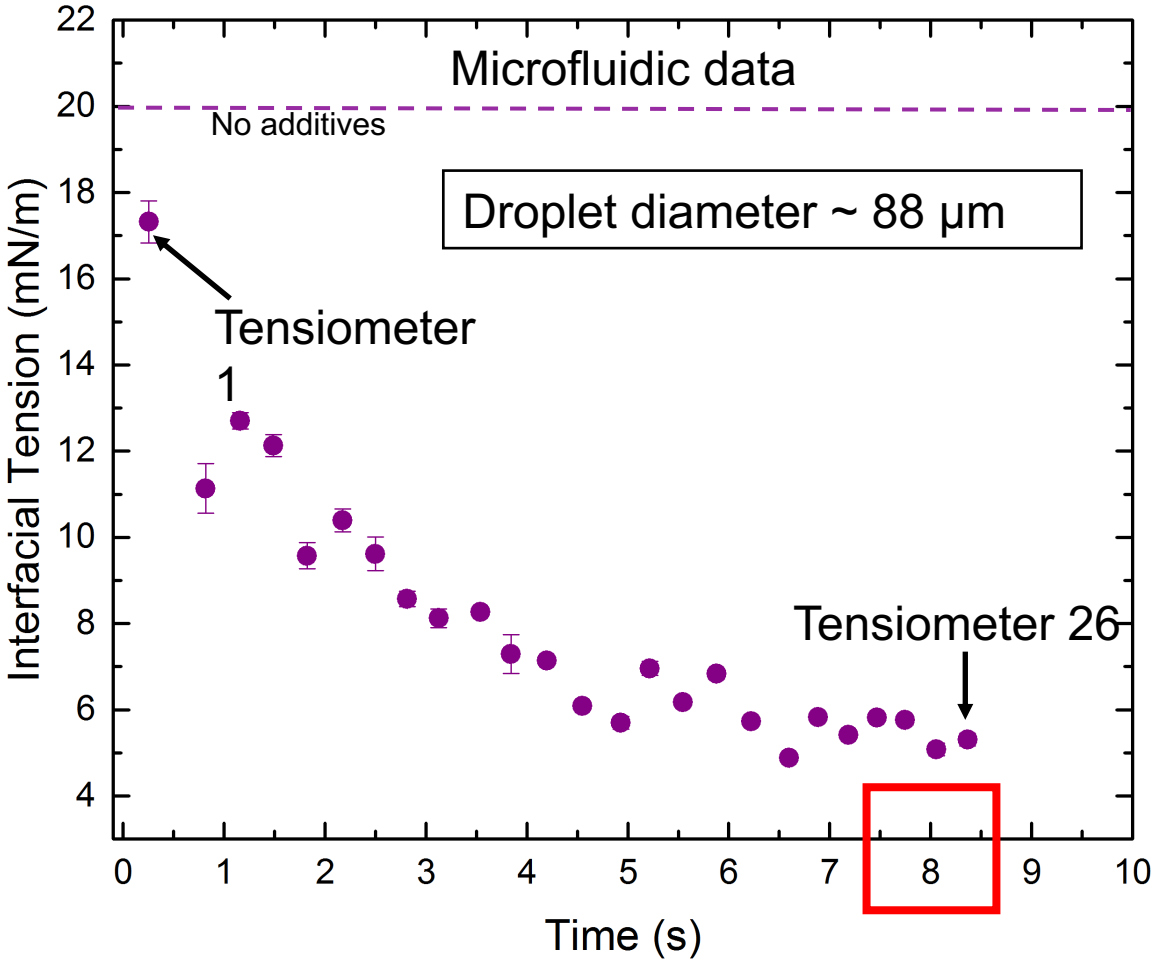


N. Alvarez, *Doctoral Dissertation* (2011)

Chevron Diesel Emission Test Fuel (ULSD)

IFT decay in **10 minute** (pendant drop) vs. **8 seconds** (microfluidics)

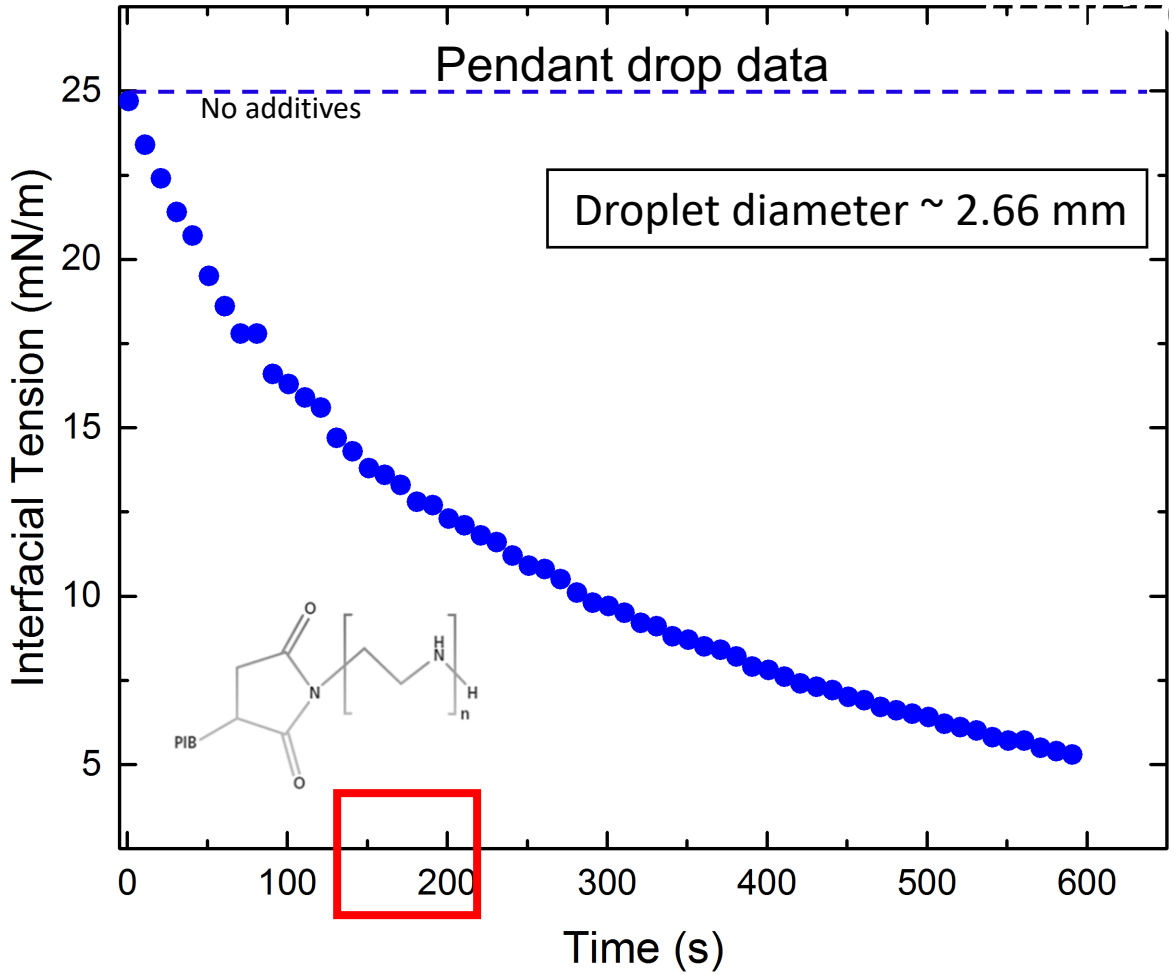


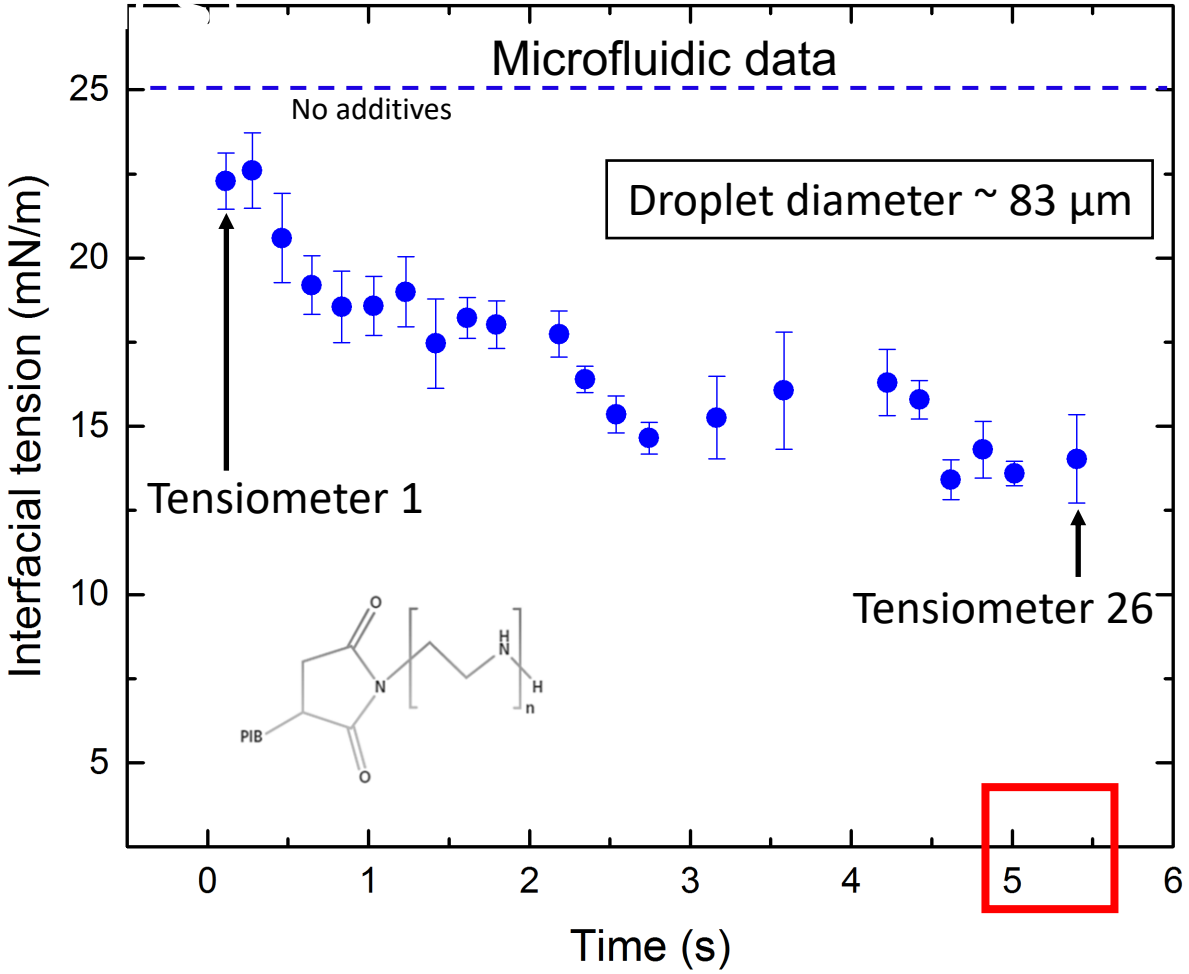


Narayan et al., *Energy and Fuels* (2018)

Model Fuel + PIBSI

IFT decay to 13 mN/m **3 mins** (pendant drop) vs. **6 seconds**

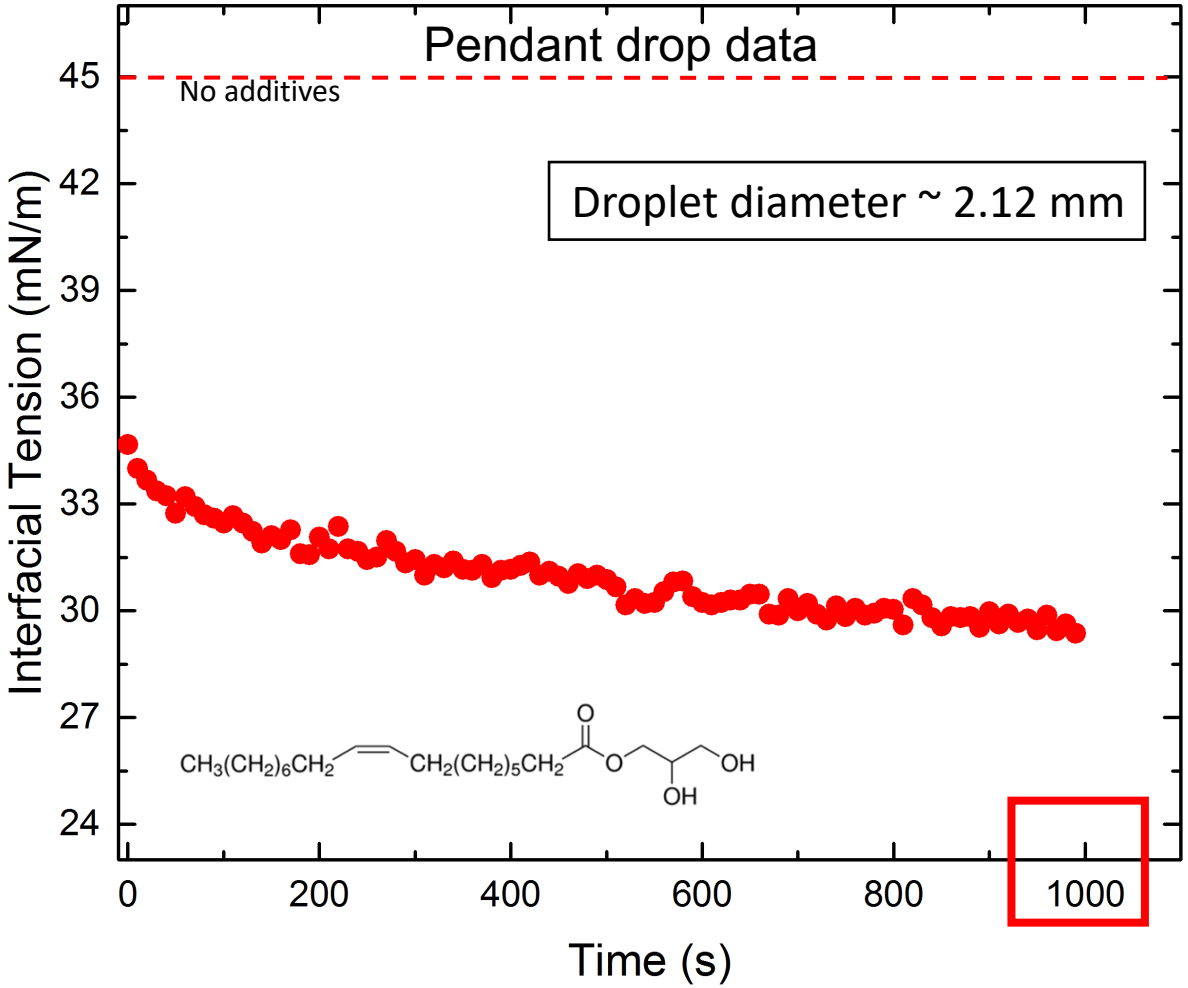


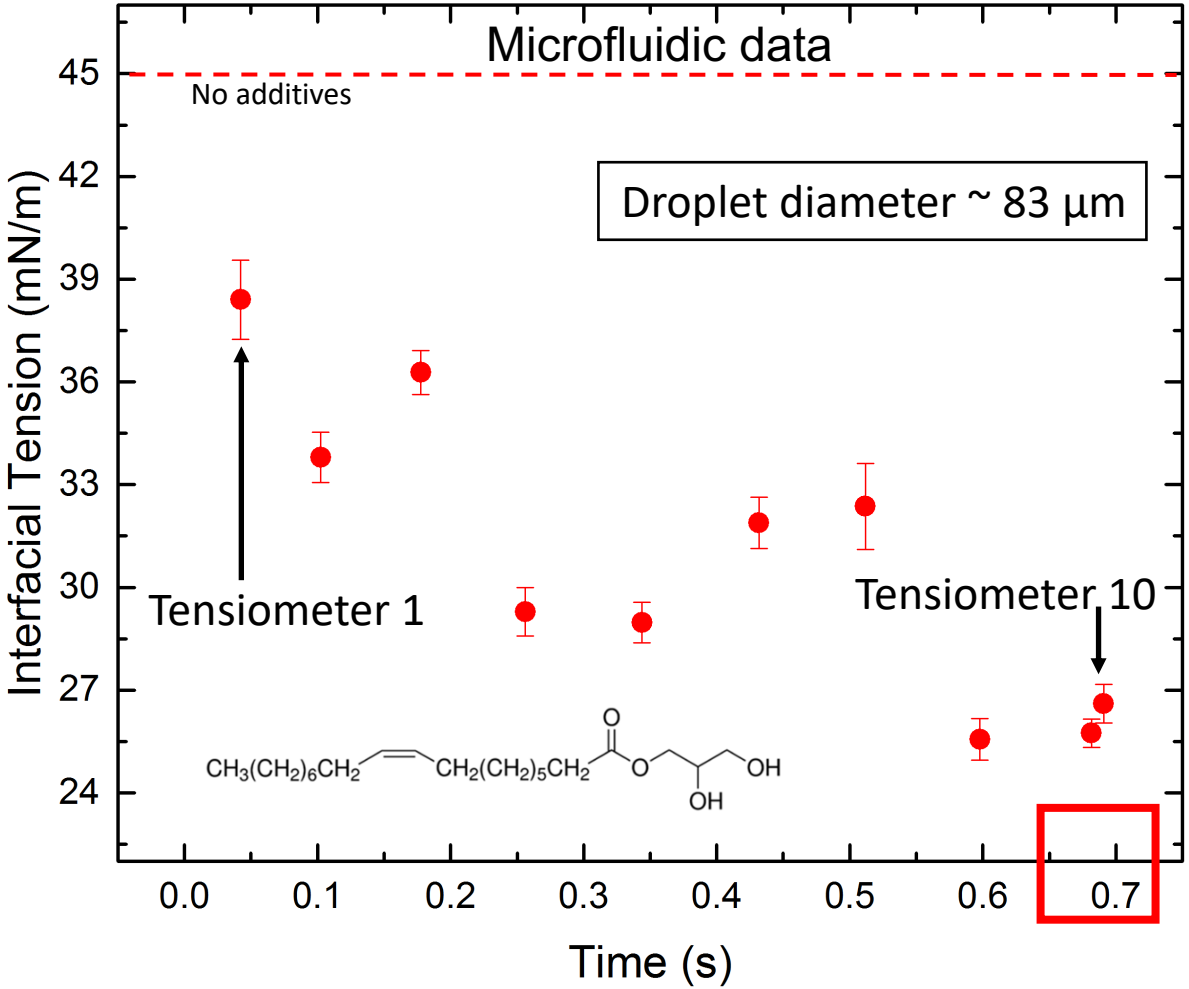


Narayan et al., *Energy and Fuels* (2018)

CT ULSD + 0.01% mg/ml monoolein

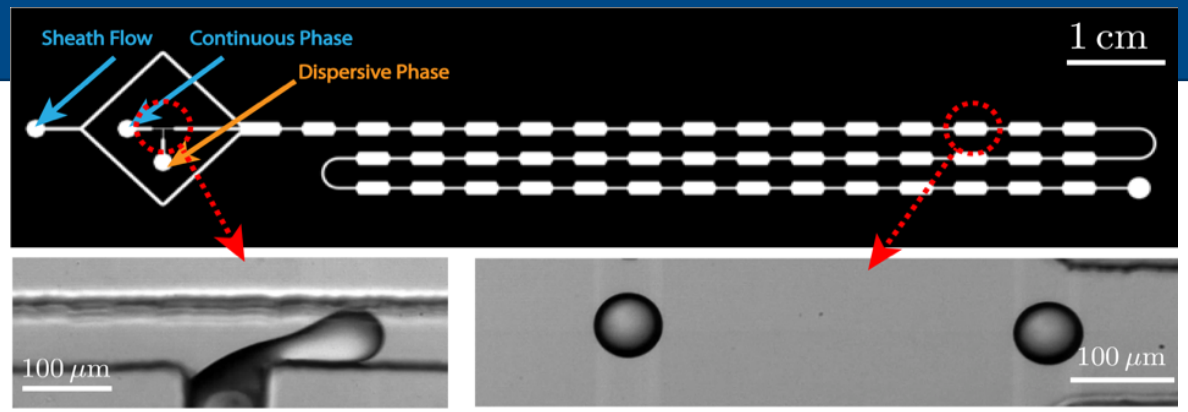
IFT decay **16 minutes** (pendant drop) vs. **<1 second** (microfluidics)





Narayan et al., *Energy and Fuels* (2018)

Simulated bilgewater systems



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25% - 2190 TEP Steam Lube Oil (MIL-PRF-17331K)	25% - Commercial Detergent Tide Ultra (liquid)
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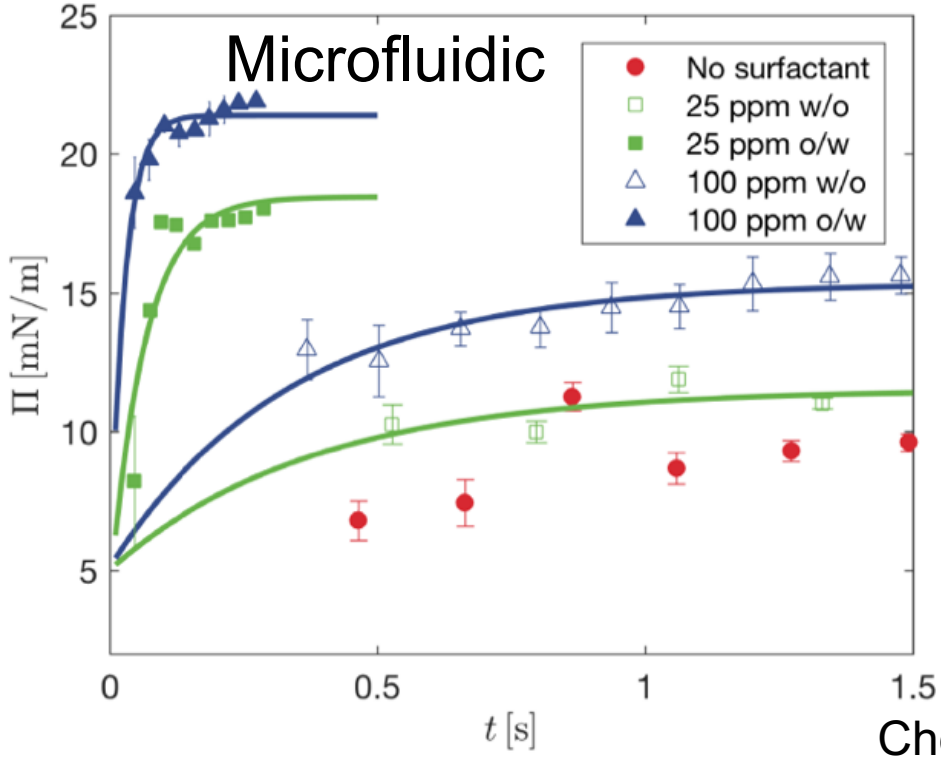
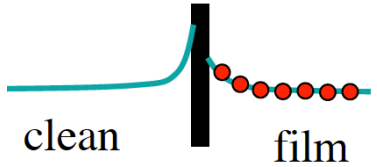
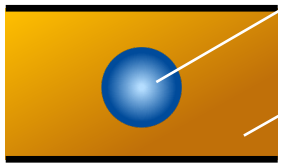


γ : Interfacial Tension: Energy per unit area

$\Pi = \gamma_{clean} - \gamma_{film}$: Surface Pressure

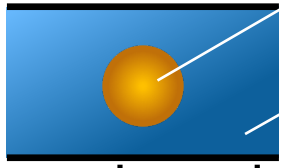




Sea water

SERDP oil mix

(open symbols)



SERDP oil mix

Sea water

(closed symbols)

Chen & Dutcher (Under Review)

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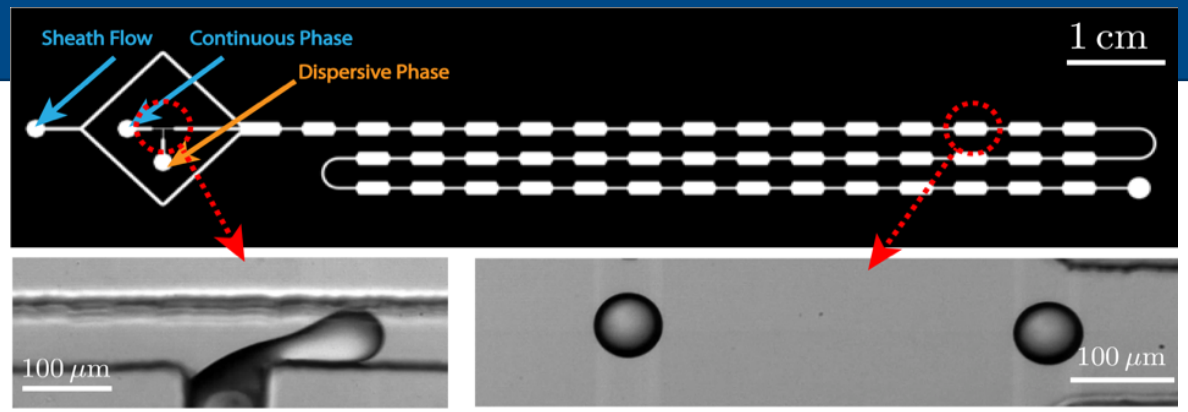
Simulated bilgewater systems



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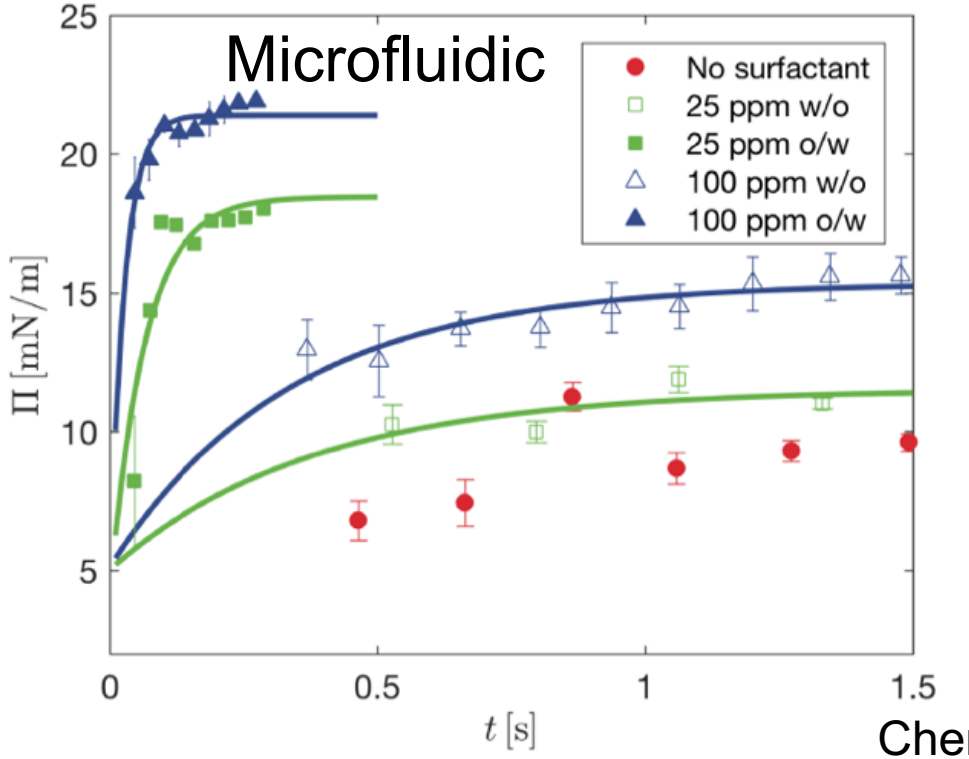

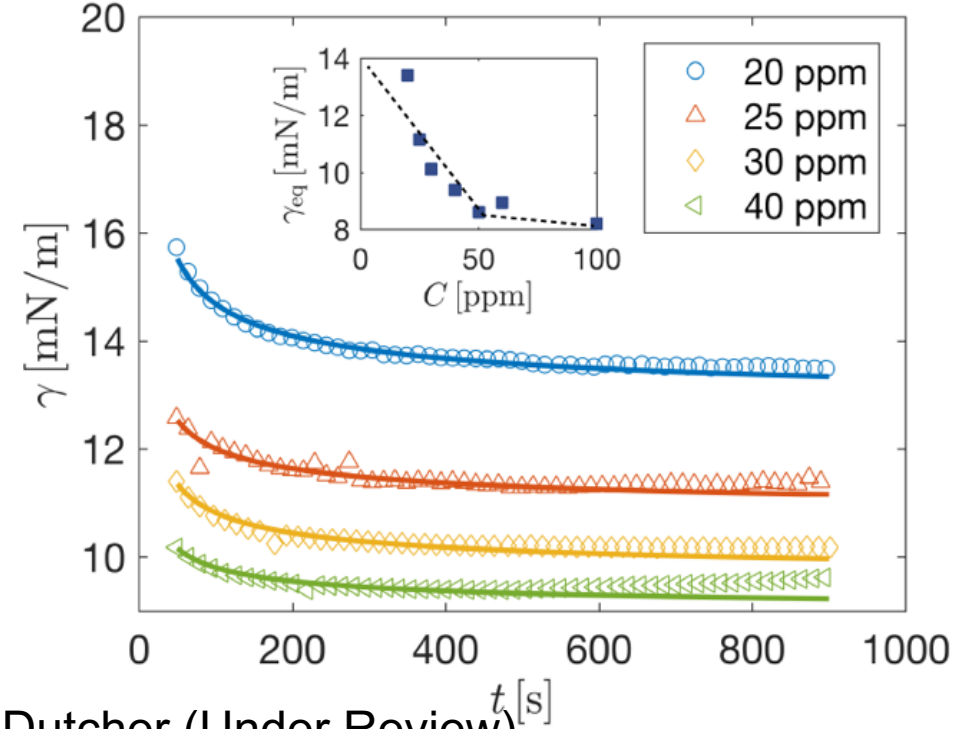

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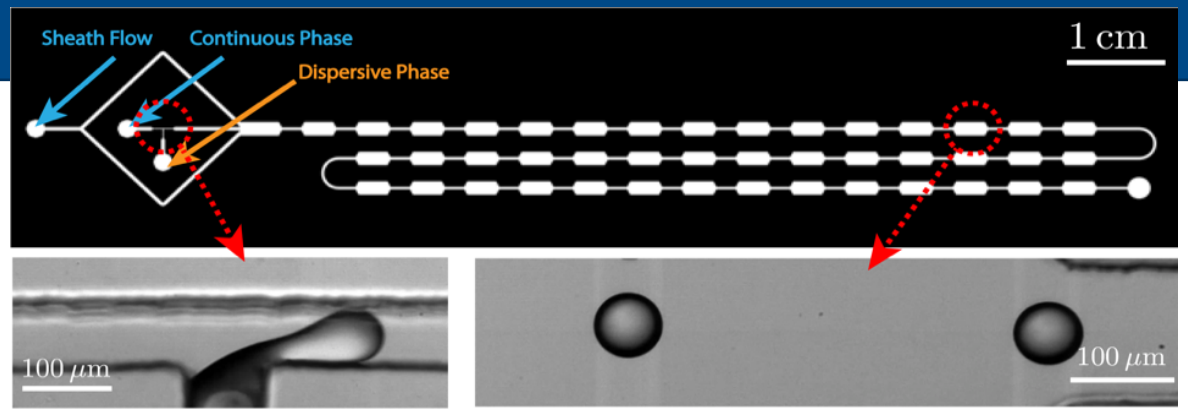

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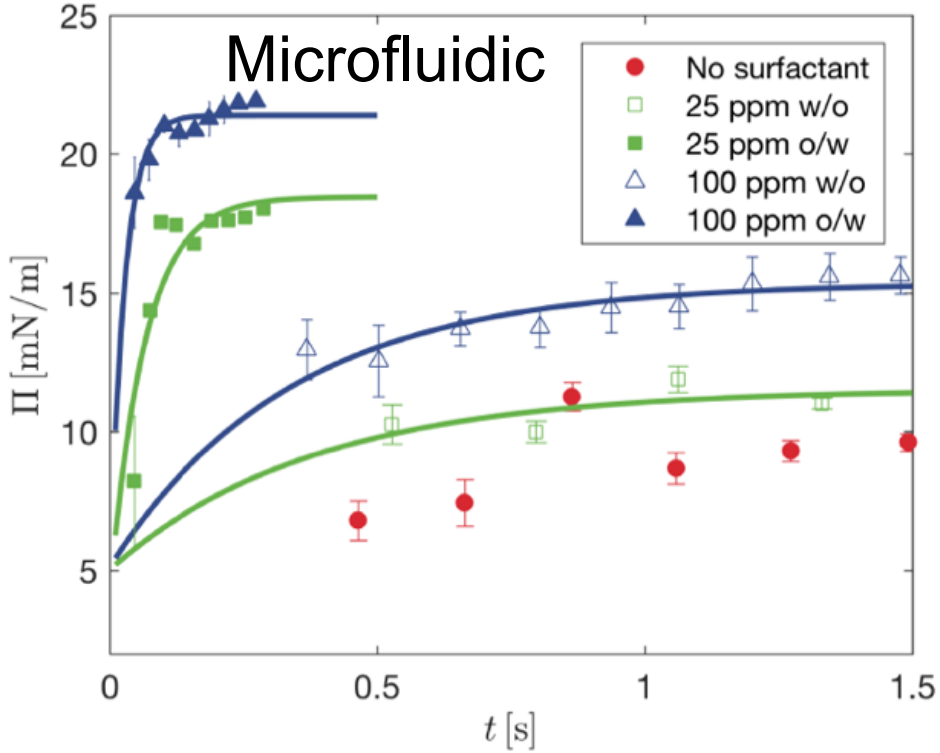

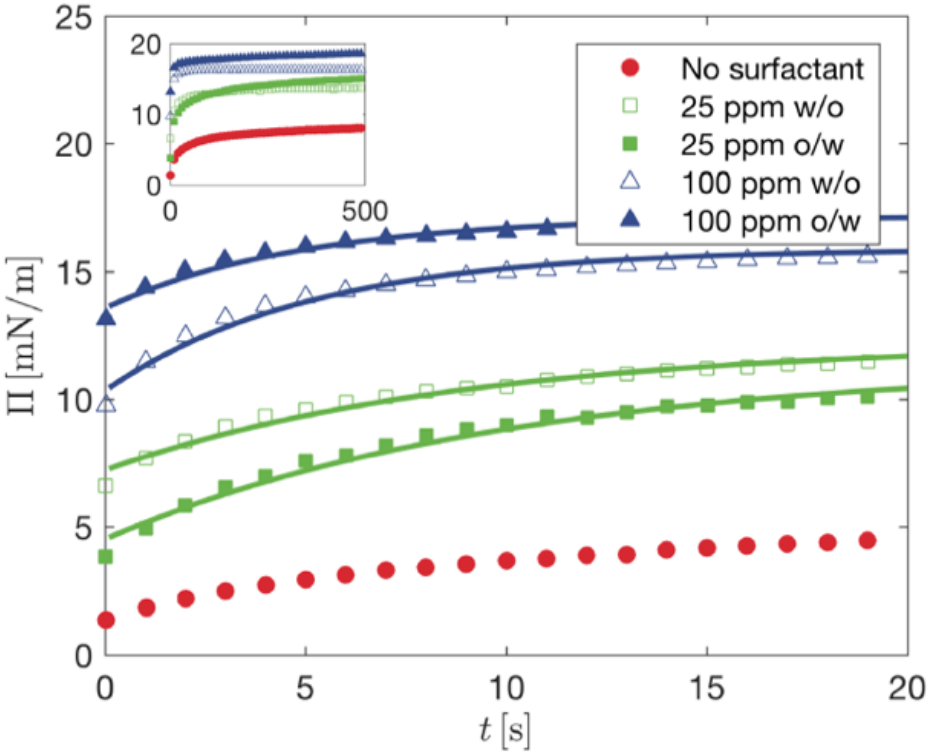

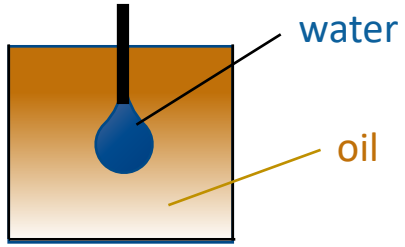

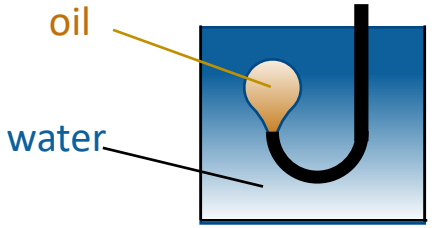

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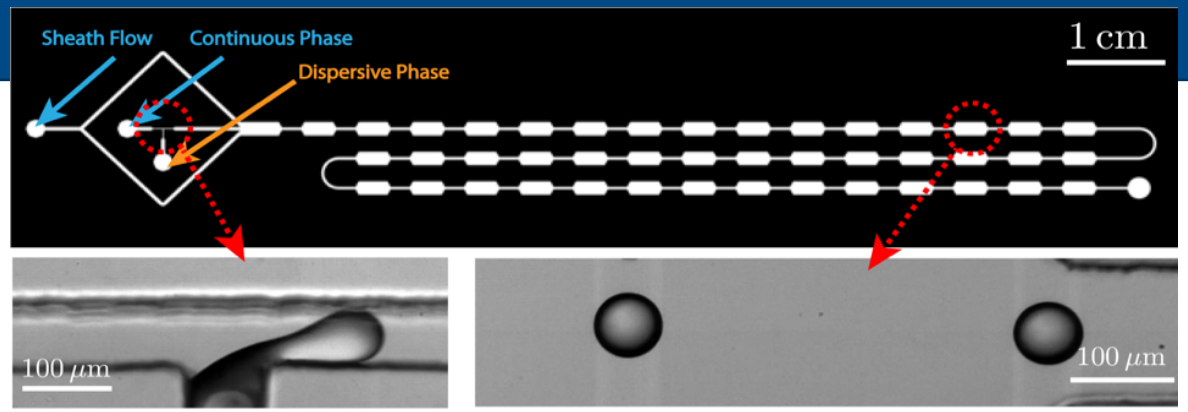

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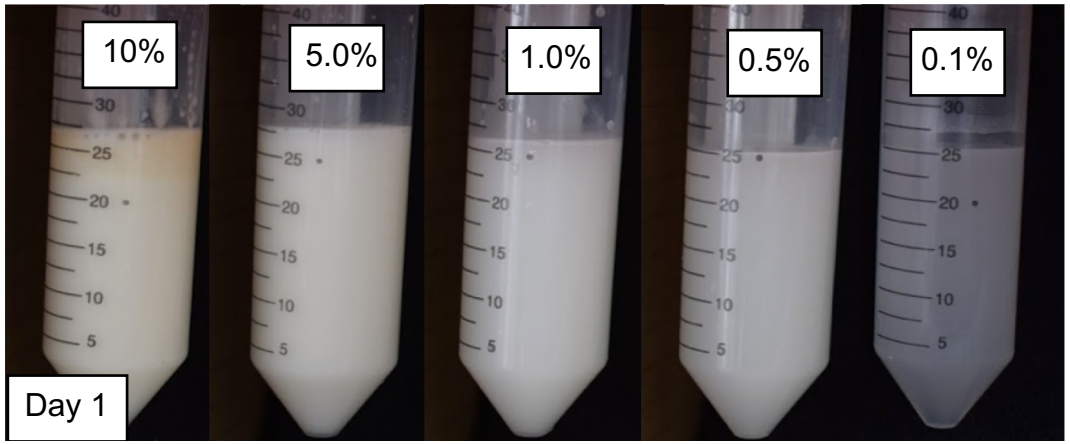
Summary of dynamic interfacial tension bilgewater measurements:

- Decay in IFT of microscale droplets much faster than macroscale droplets (i.e., microscale droplets are more stable)
- Phase does <u>not</u> matter for millimeter drops. Large drops always diffusion-limited (Surfactant transport scale 15 s for both inner and outer phase).
- Phase <u>does</u> matter for microscale droplets. Both diffusion and adsorption timescales important (0.38 s for outer phase; 0.065 s for inner phase)

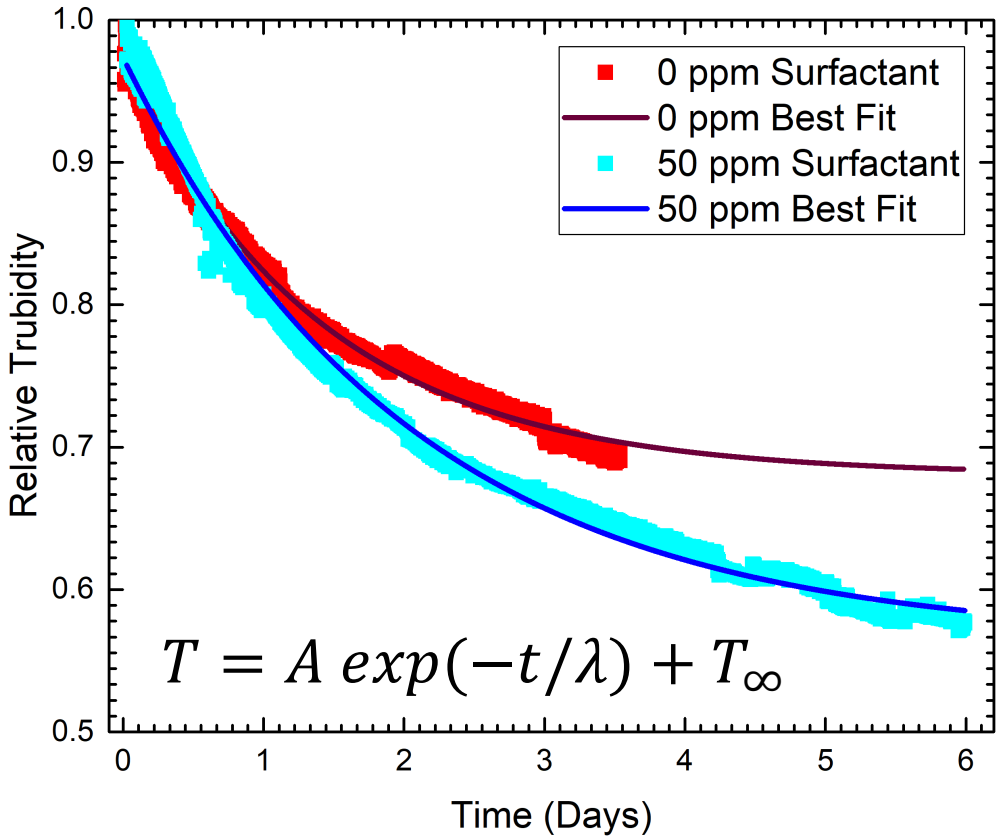
Microscale bulk stability: Oil separation

Stability tests: Phase separation; Turbidity change



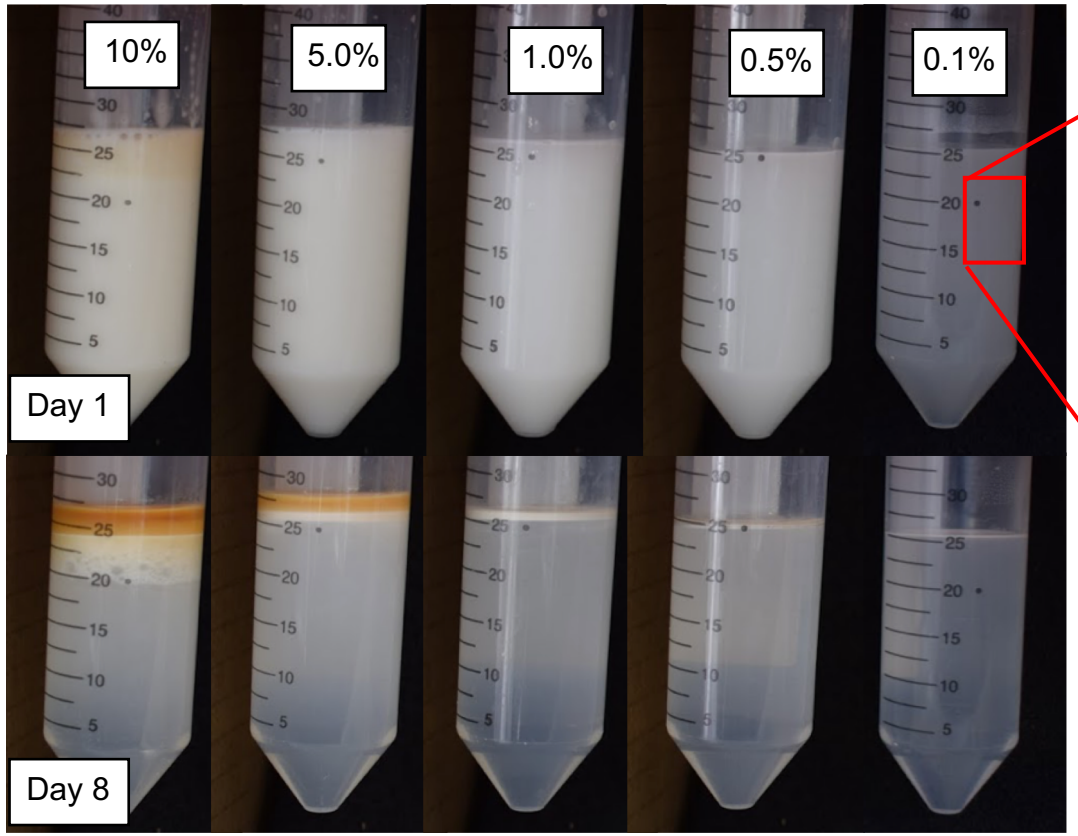
On the macroscale, see phase separation and drop in turbidity (varied: oil type & content, surfactant type & concentration, salinity)

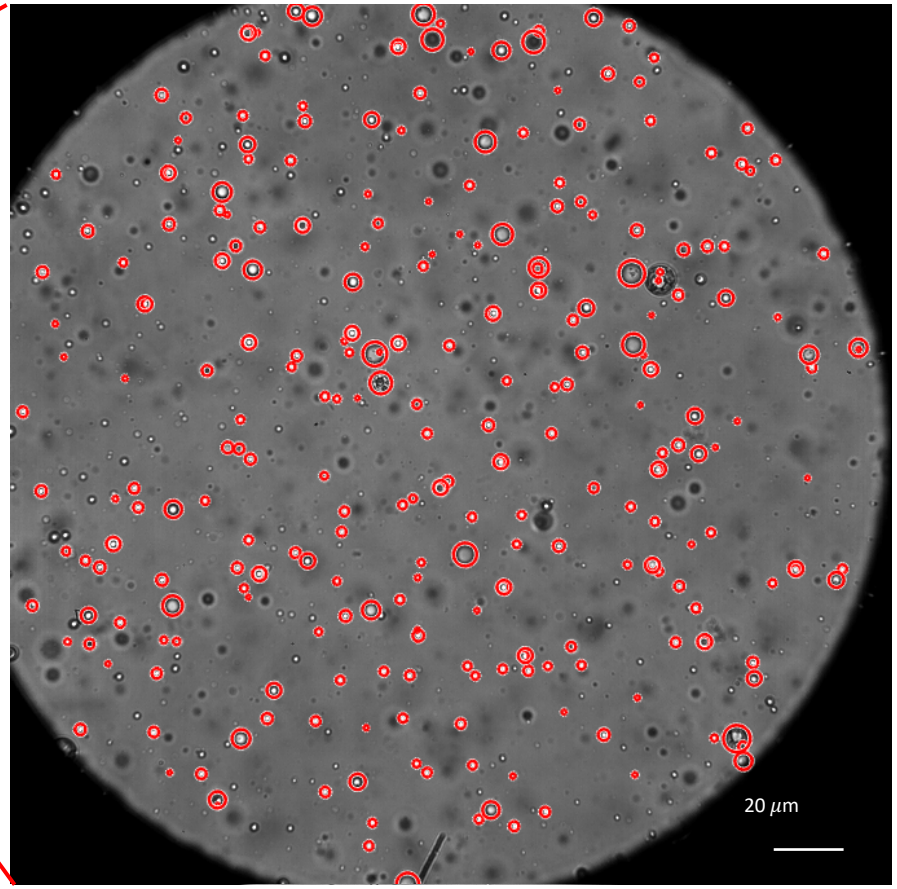
Determine destabilization timescales



Destabilization: Change in size distribution

Stability tests: Phase separation; Turbidity change



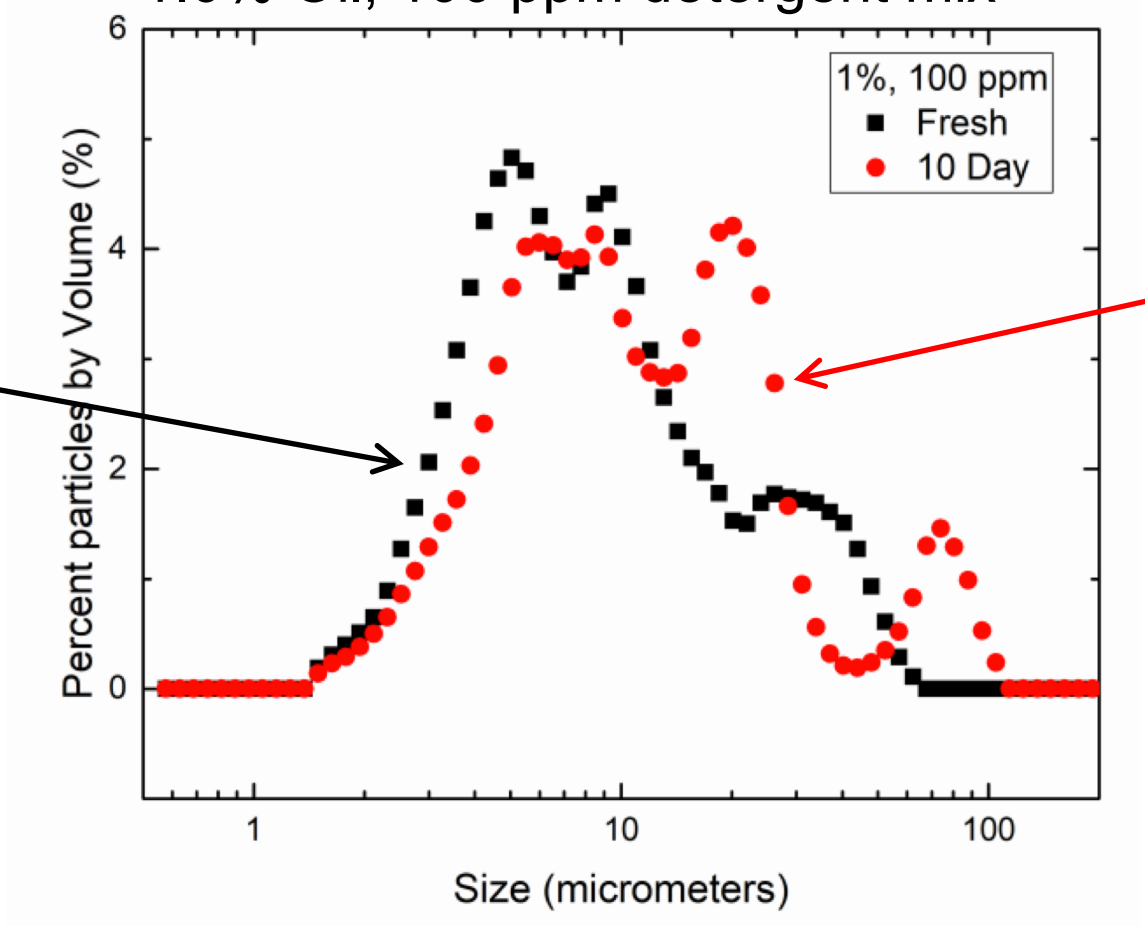


0.1% Oil, 100 ppm detergent mix

Partial destabilization over long periods of time

Fresh: More droplets, smaller average size

1.0% Oil, 100 ppm detergent mix



10 Days: Fewer droplets, larger average size

Summary and Acknowledgements

Summary:

- Microfluidic measurements for **dynamic interfacial tension**, **surfactant mass transfer rates** and **coalescence**.
- Macroscale measurements for coalescence-based **destabilization during flow**.

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