Carnegie Mellon Center for Complex Fluids Engineering

Electrohydrodynamics of emulsion droplets

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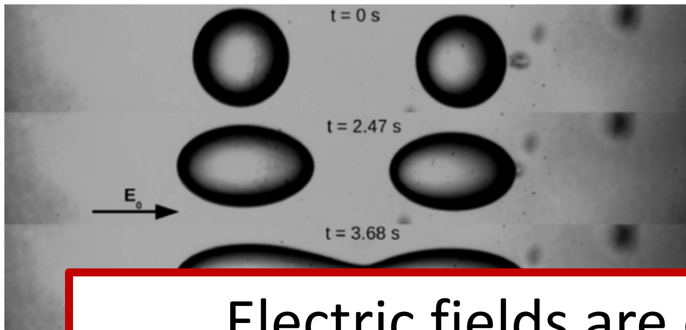
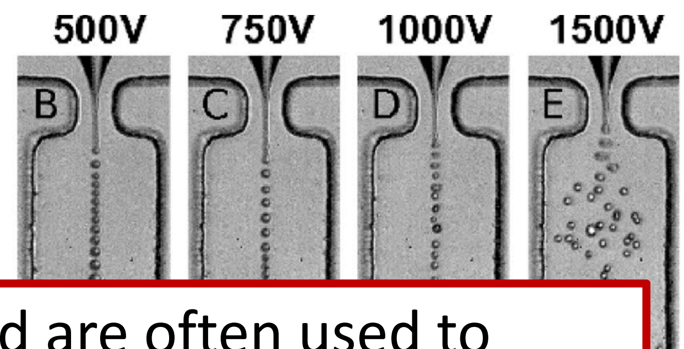
Surfactant-laden fluid-fluid interfaces under electric fields

Electrocoalescence of Drops

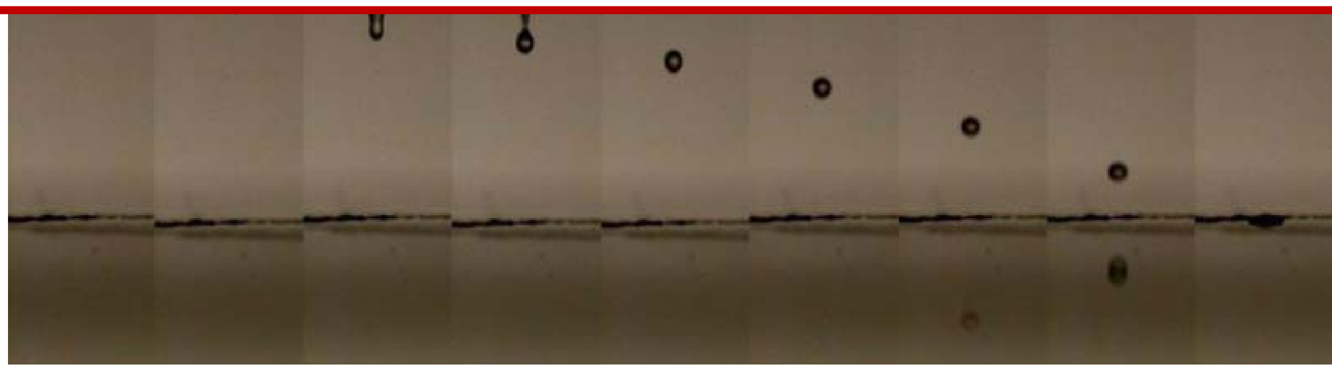


Electroemulsification



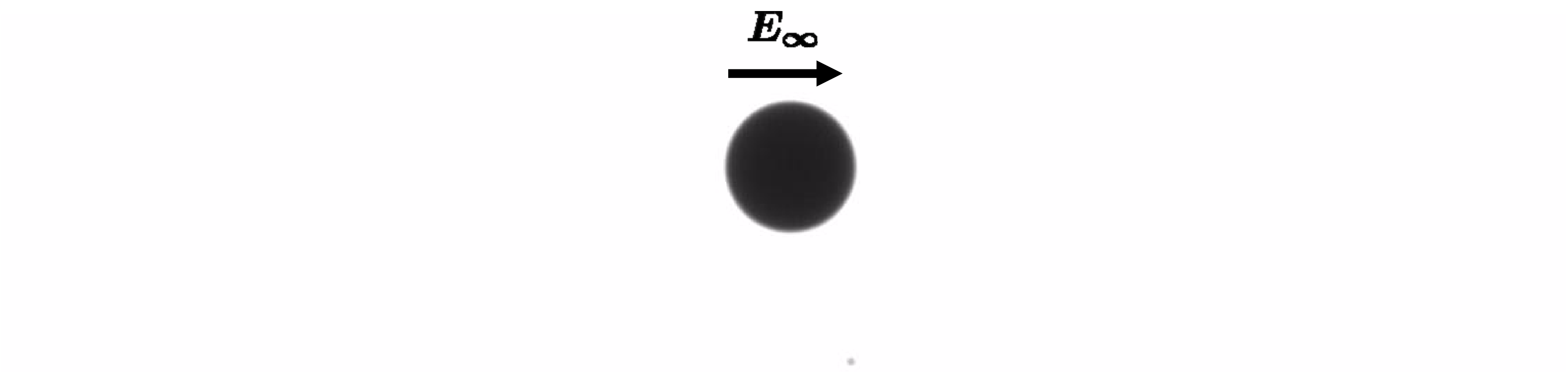
Electric fields are efficient and are often used to manipulate fluid drops.

We started to think about the impact of particles, polymers and surfactants.



Kang *et al.* (2011)

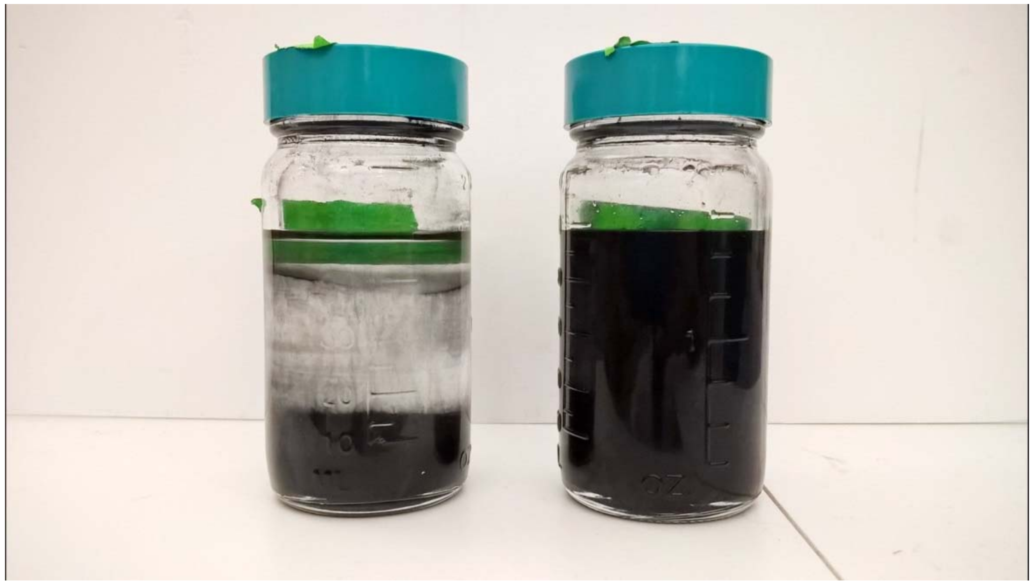
Suspension Loaded Drops



Squalane drop with 3.3 g/L carbon black particles + 2pph OLOA in silicone oil

What causes this breakup?

Drop: Carbon black particles suspended in squalane



Particles: Monarch 280 carbon black

Primary particle size: 30 nm

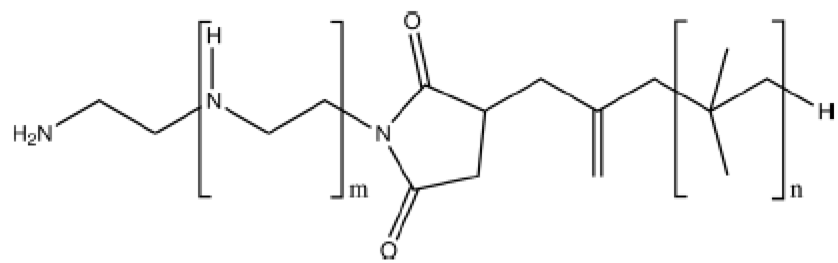
Primary aggregate size: 200 nm

3.3 g/L carbon black (fixed)

0.2% volume fraction

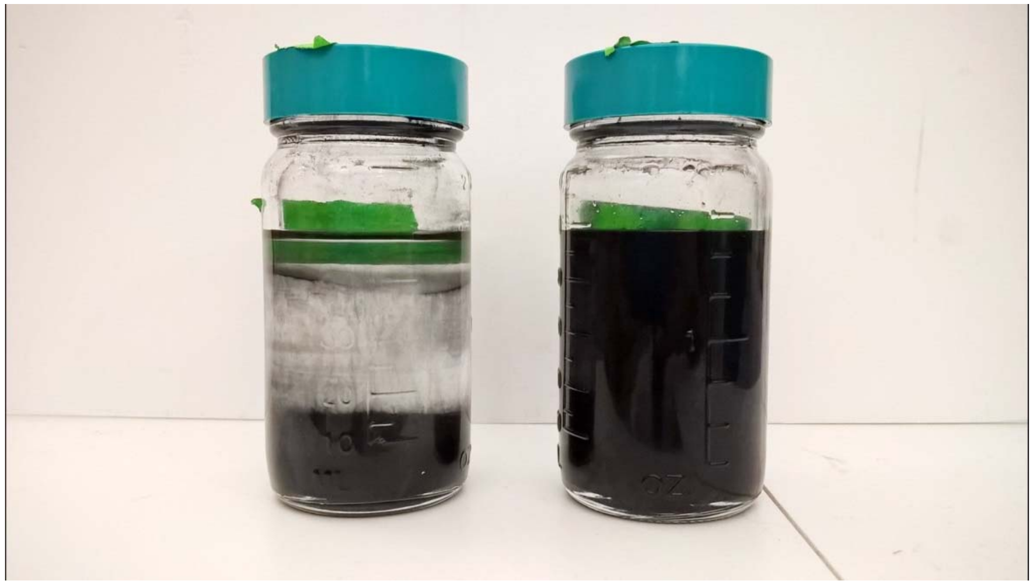
Surfactant: Polyisobutylene succinimide

OLOA 11000



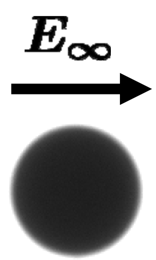
Smith and Eastoe (2012)

Surfactant concentration affects suspension stability



2 pph OLOA
(unstable: steric)

30 pph OLOA
(stable: electrostatic)

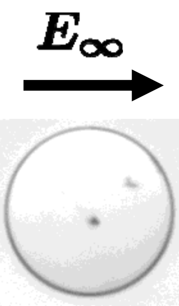


__Goal:__ How does suspension stability affect drop breakup?

Bleier et al., J Colloid and Interface Sci 2017

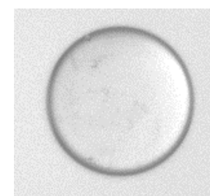
Roadmap of experiments

Medium phase: Silicone oil (5000 cSt)



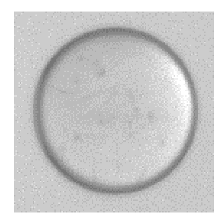
Pure squalane

30 pph OLOA
(stable suspension)



Equivalent OLOA (0.12 wt%)
No particles

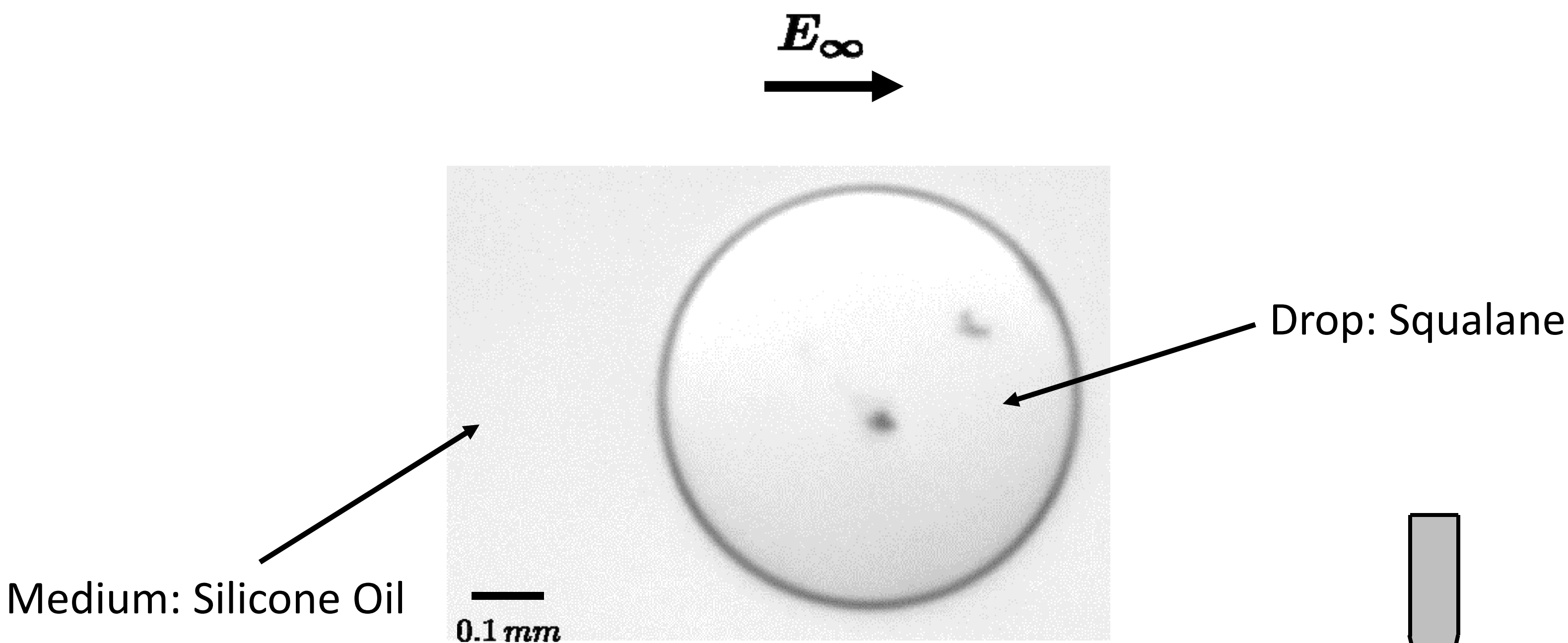
2 pph OLOA
(unstable suspension)



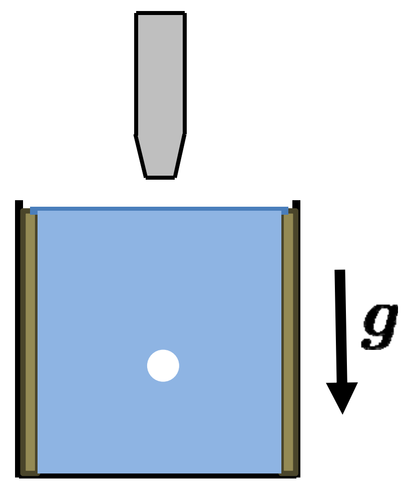
Equivalent OLOA (0.008 wt%)
No particles

Pure squalane drop breaks via tip streaming

Drop of squalane in silicone oil – *7.6 kV/cm*

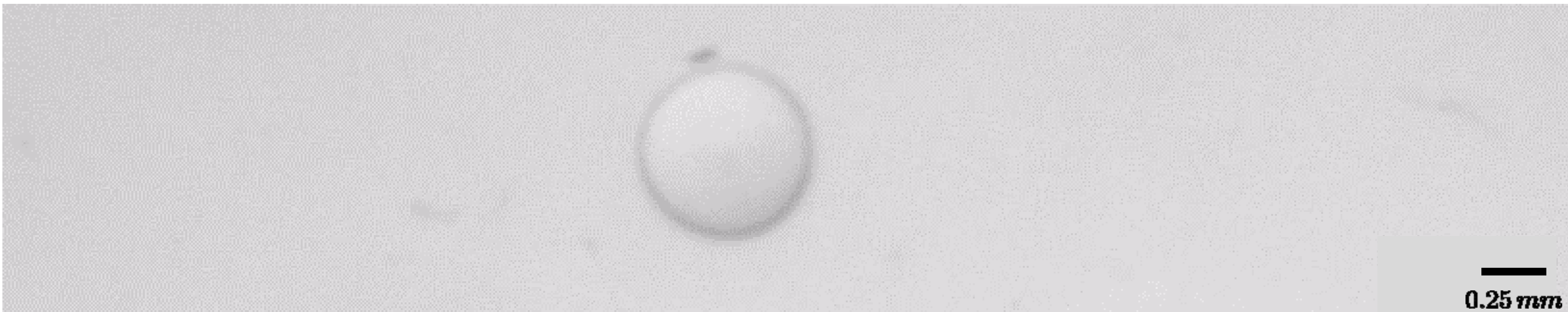


Breakup mode: *Tip streaming*



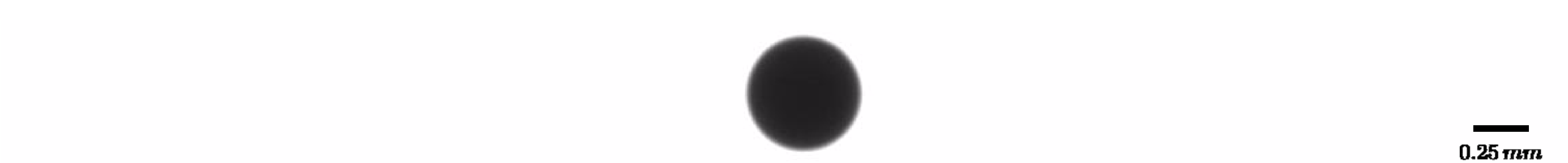
Drop containing a stable colloidal suspension

$$E_\infty = 2.5kV/cm$$



30 pph equivalent OLOA
No particles

$$E_\infty = 2.5kV/cm$$



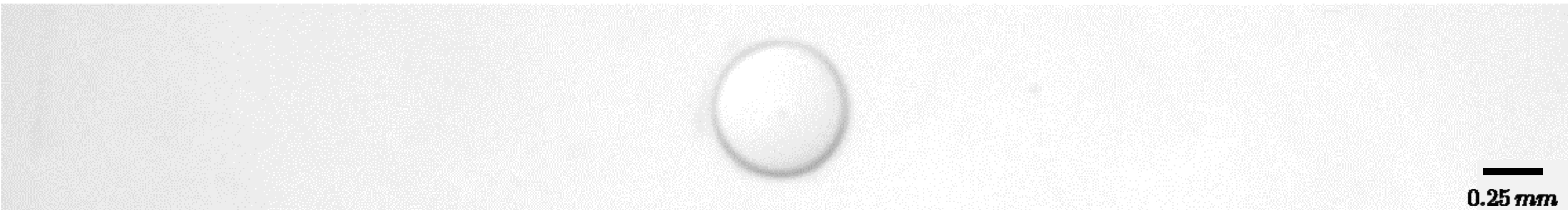
30 pph OLOA
(stable)

Breakup mode: *End pinching*

Particles do not qualitatively change breakup mode

Non-axisymmetric breakup at larger field

$$E_\infty = 5.3kV/cm$$



30 pph equivalent OLOA

No particles

$$E_\infty = 5.3kV/cm$$

30 pph OLOA

(stable)

Breakup mode: *Charged lobe disintegration*

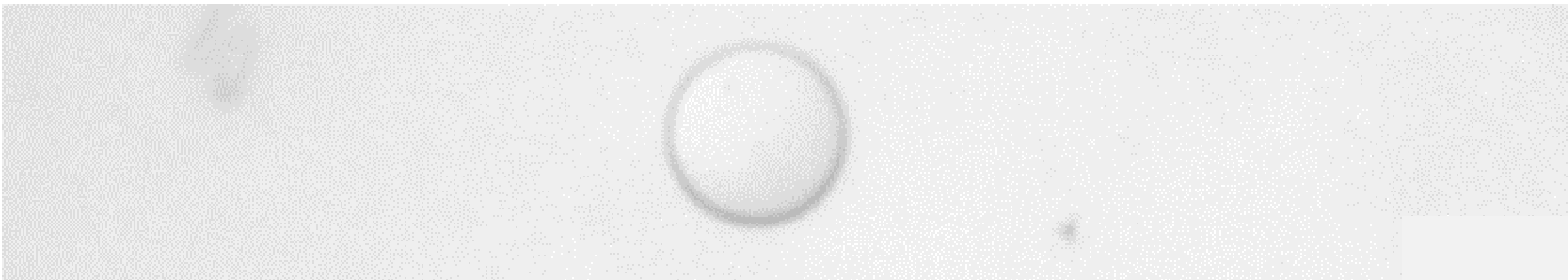
Again, particles do not qualitatively change breakup mode

Karyappa et al., JFM 2014

Drop containing an unstable colloidal suspension

$$E_\infty = 2.5kV/cm$$

→



2 pph equivalent OLOA
No particles

Breakup mode: *End pinching*

$$E_\infty = 2.5kV/cm$$

→

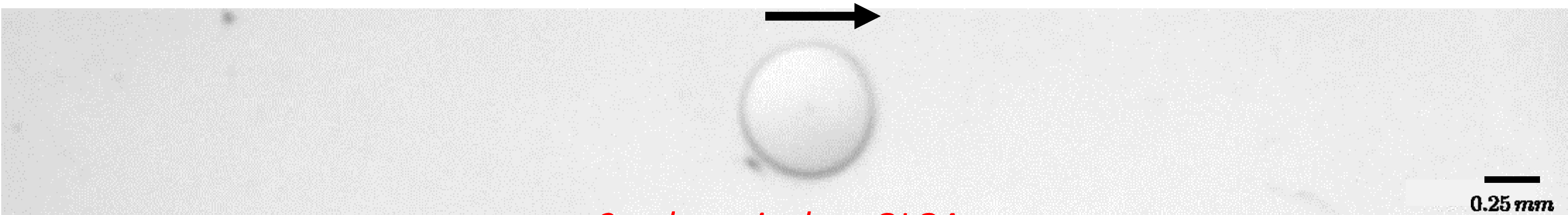
2 pph OLOA
(unstable)

Non homogeneous breakup

Particles *do* qualitatively change breakup mode

Unstable suspension at larger field

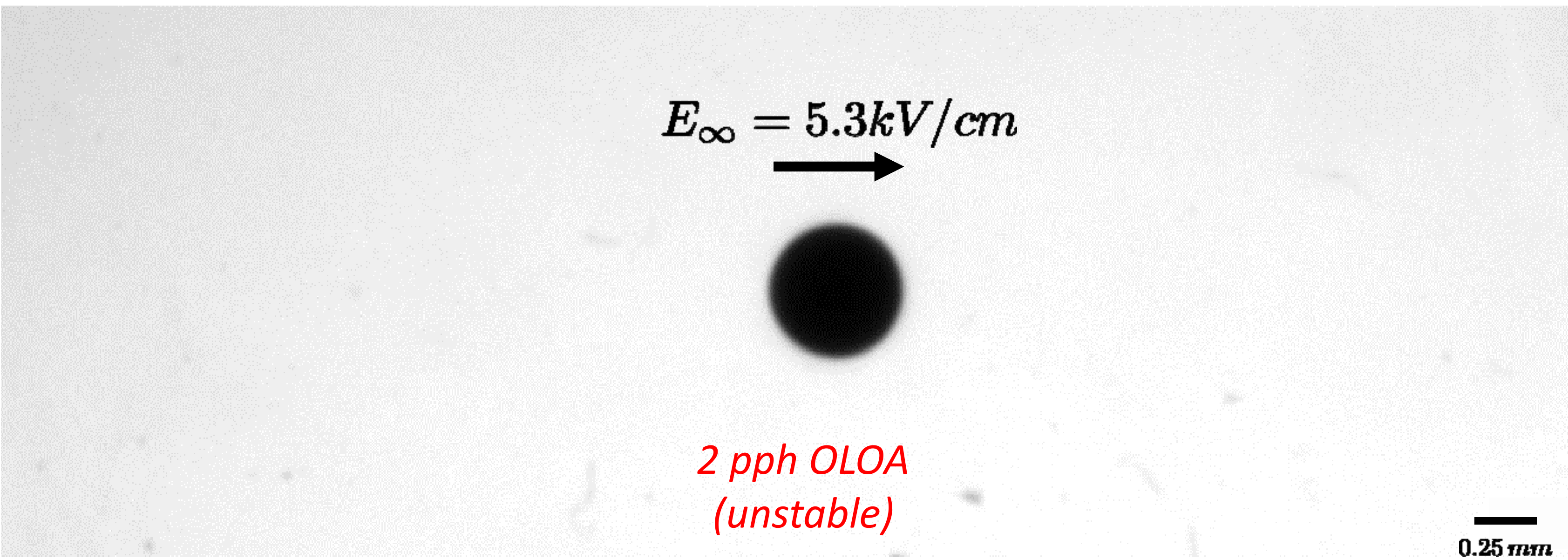
$E_\infty = 5.3kV/cm$



2 pph equivalent OLOA

No particles

Breakup mode: *End pinching*



Unstable suspension again yields non homogeneous breakup

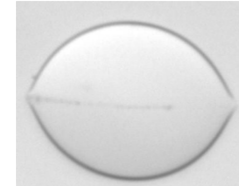
Summary of experiments

	$2.5\,kV/cm$	$5.3\,kV/cm$	$7.6\,kV/cm$

Pure squalane

No breakup

No breakup



Tip streaming

Transition

30 pph OLOA

End pinching

Charged lobe disintegration

30 pph (Stable)

End pinching

Charged lobe disintegration

Qualitatively Same

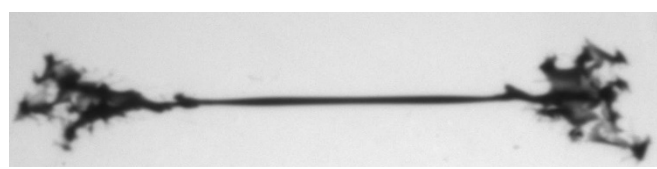
2 pph OLOA

End pinching

End pinching

2 pph (Unstable)

Non homogeneous

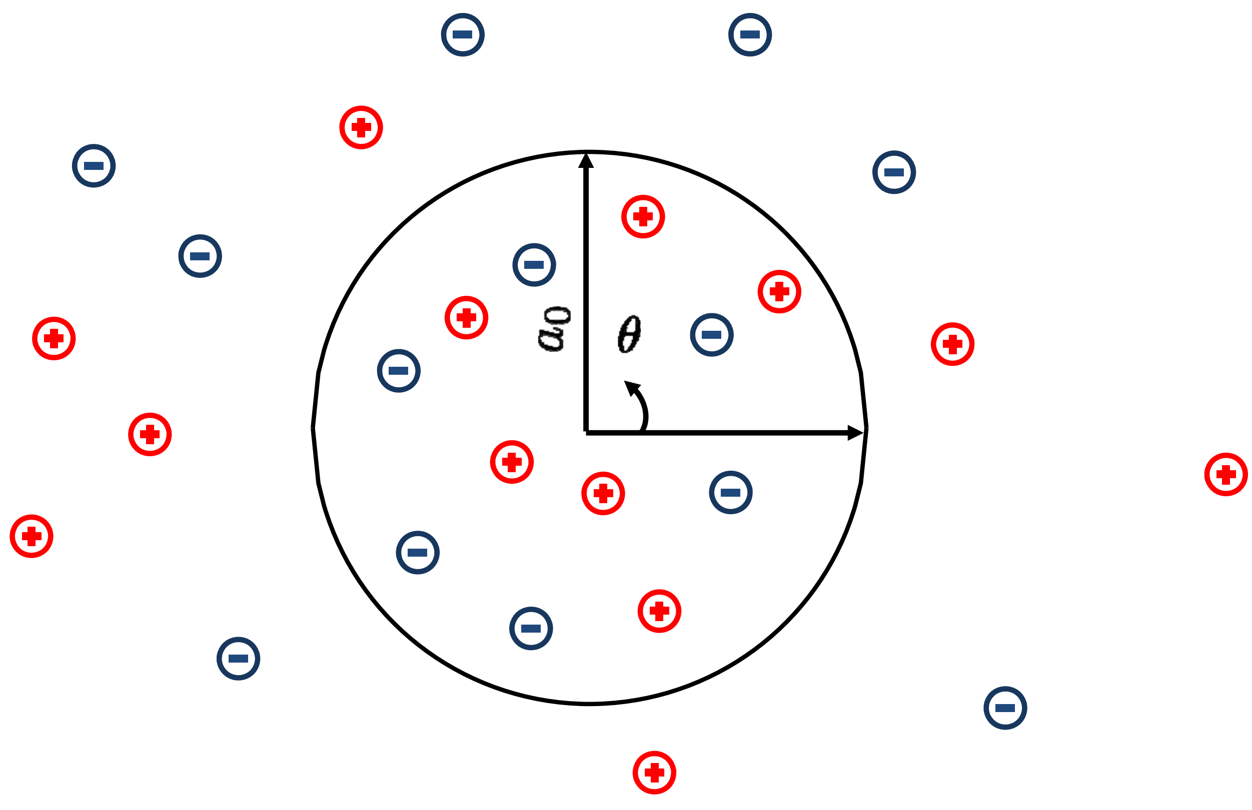


Non homogeneous

Qualitatively Different

Leaky Dielectric Model

- Small electrical conductivity (impurity); bulk is electroneutral

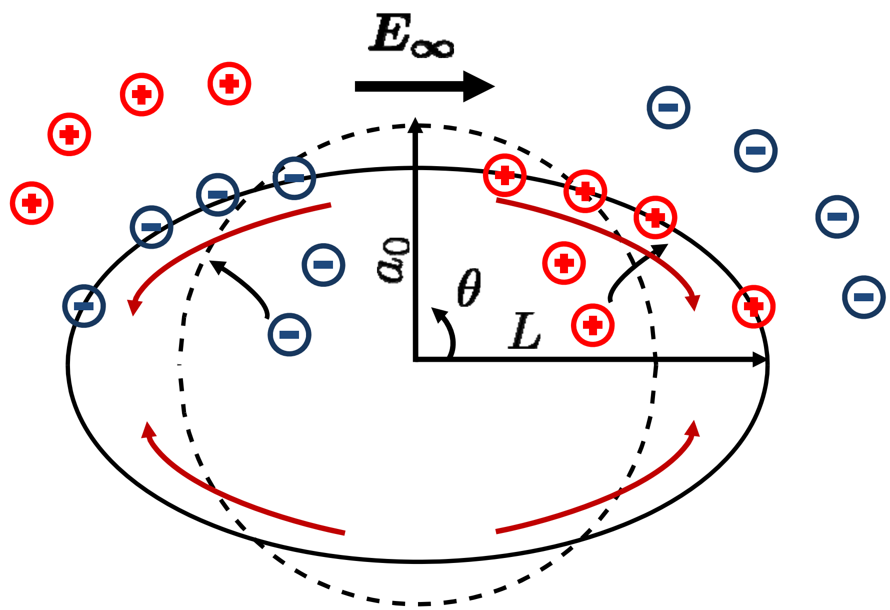


An undeformed drop

Taylor, 1966

Leaky Dielectric Model

- Interface is charged under an electric field
- Electric traction acts along the interface and deforms the drop
- Drop breaks above a critical field



Deformation, $D = L/a_0$

Final state of the drop = $f(M = \frac{\mu_i}{\mu_o}, S = \frac{\varepsilon_i}{\varepsilon_o}, R = \frac{\sigma_o}{\sigma_i}, Ca_E = \frac{a_0 \varepsilon_o E_\infty^2}{\gamma}, Re_E = \frac{\varepsilon_o^2 E_\infty^2}{\mu_o \sigma_o})$

Boundary Integral Computations to predict drop deformation

Taylor, 1966

Computing nonlinear deformation

Boundary Integral Method: Convert differential equations in the domain to integral equations along the boundary

Electric Field

$$\nabla^2 \phi = 0$$

Jump in Normal Field

$$\frac{1}{S} E_{n,o} - E_{n,i} = \frac{1}{S} q$$

Interfacial Charge Transport

$$\frac{1}{R} E_{n,i} - E_{n,o} = \frac{Re_E}{Ca_E} \frac{\partial q}{\partial t} + Re_E \nabla_s \cdot (\boldsymbol{u} q)$$

Fluid Flow

$$\nabla^2 \boldsymbol{u} = \nabla p \qquad \nabla \cdot \boldsymbol{u} = 0$$

Lanauze et al., 2015

Computing nonlinear deformation

Boundary Integral Method: Convert differential equations in the domain to integral equations along the boundary

Electric Field

$$\boldsymbol{E}^{\infty} \cdot \boldsymbol{n} + \frac{1}{4\pi} \oint_A \frac{\boldsymbol{r} \cdot \boldsymbol{n}}{r^3} \Delta E_n dA = \frac{1}{2}(E_{n,o} + E_{n,i})$$

Jump in Normal Field

$$\frac{1}{S} E_{n,o} - E_{n,i} = \frac{1}{S} q$$

Interfacial Charge Transport

$$\frac{1}{R} E_{n,i} - E_{n,o} = \frac{Re_E}{Ca_E} \frac{\partial q}{\partial t} + Re_E \nabla_s \cdot (\boldsymbol{u} q)$$

Fluid Flow

$$\boldsymbol{u}_o = -\frac{1}{4\pi(M+1)} \oint_A \Delta \boldsymbol{f} \cdot \boldsymbol{J} \, dA + \frac{3}{2\pi} \frac{M-1}{M+1} \oint_A \boldsymbol{u}_o \cdot \boldsymbol{K} \cdot \boldsymbol{n} \, dA$$

$$A = \text{drop surface}$$

Lanauze et al., 2015

Nonlinear deformation with insoluble surfactant

Boundary Integral Method: Convert differential equations in the domain to integral equations along the boundary

Electric Field

$$\boldsymbol{E}^{\infty} \cdot \boldsymbol{n} + \frac{1}{4\pi} \oint_A \frac{\boldsymbol{r} \cdot \boldsymbol{n}}{r^3} \Delta E_n dA = \frac{1}{2}(E_{n,o} + E_{n,i})$$

Jump in Normal Field

$$\frac{1}{S} E_{n,o} - E_{n,i} = \frac{1}{S} q$$

Interfacial Charge Transport

$$\frac{1}{R} E_{n,i} - E_{n,o} = \frac{Re_E}{Ca_E} \frac{\partial q}{\partial t} + Re_E \nabla_s \cdot (\boldsymbol{u} q)$$

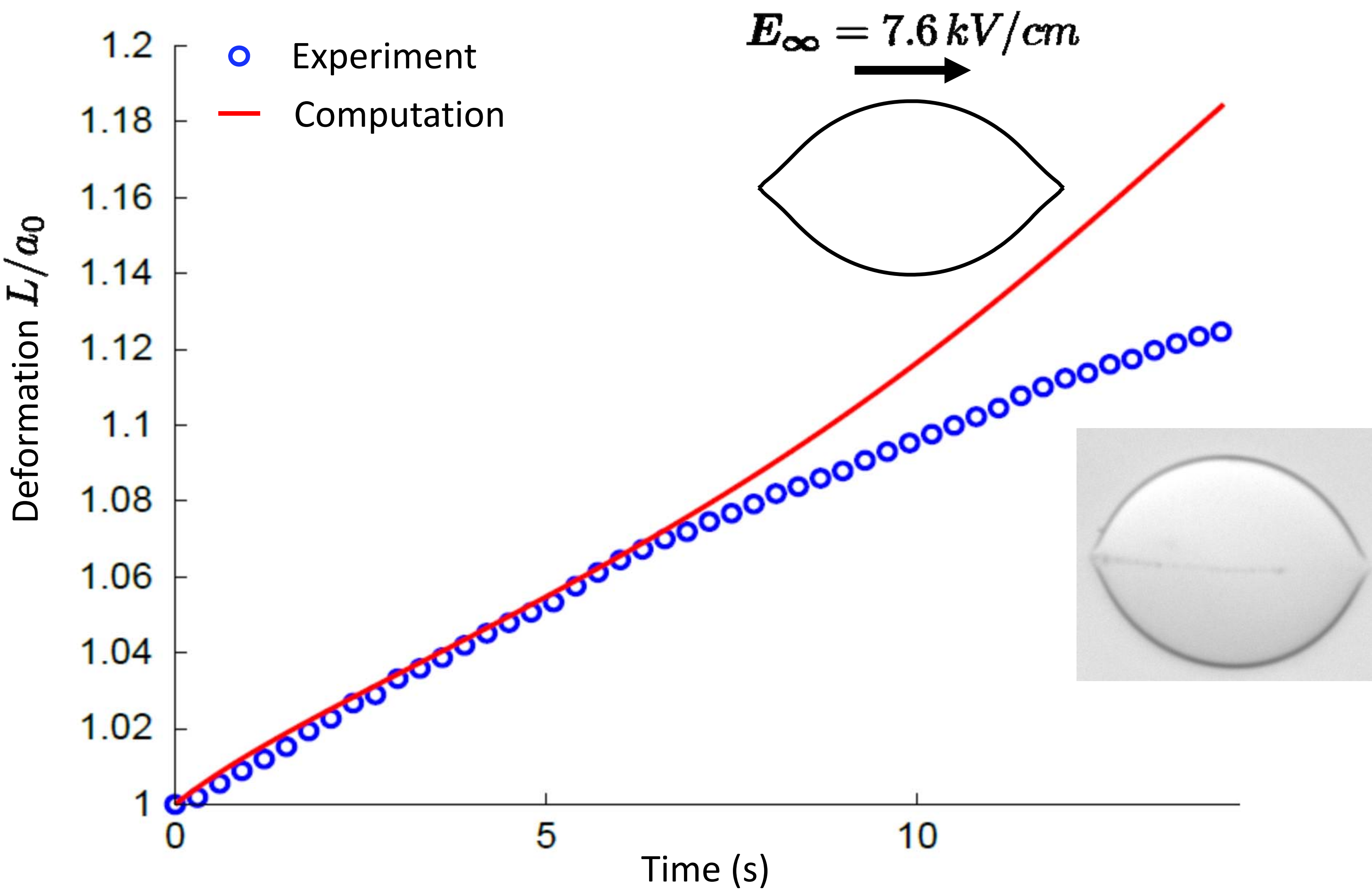
Fluid Flow

$$\boldsymbol{u}_o = -\frac{1}{4\pi(M+1)} \oint_A \Delta \boldsymbol{f} \cdot \boldsymbol{J} \, dA + \frac{3}{2\pi} \frac{M-1}{M+1} \oint_A \boldsymbol{u}_o \cdot \boldsymbol{K} \cdot \boldsymbol{n} \, dA$$

Surfactant Transport

$$\frac{1}{Ca_E} \frac{\partial \Gamma}{\partial t} + \boldsymbol{\nabla}_s \cdot (\boldsymbol{u}_s \Gamma) + (\boldsymbol{u}_s \cdot \hat{\boldsymbol{n}}) \kappa \Gamma - \frac{1}{Pe_s} \nabla_s^2 \Gamma = 0$$

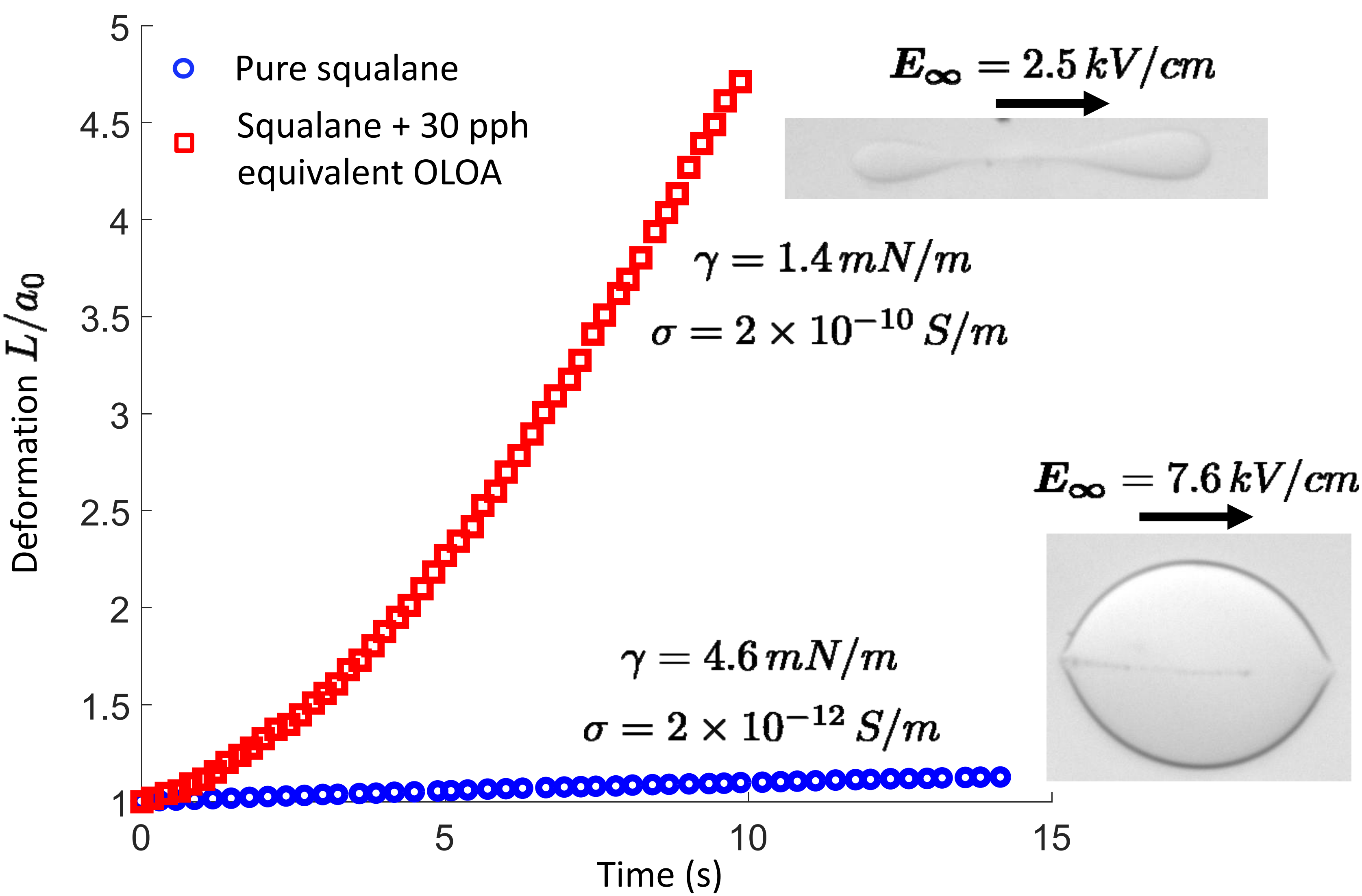
Pure Squalane Drop



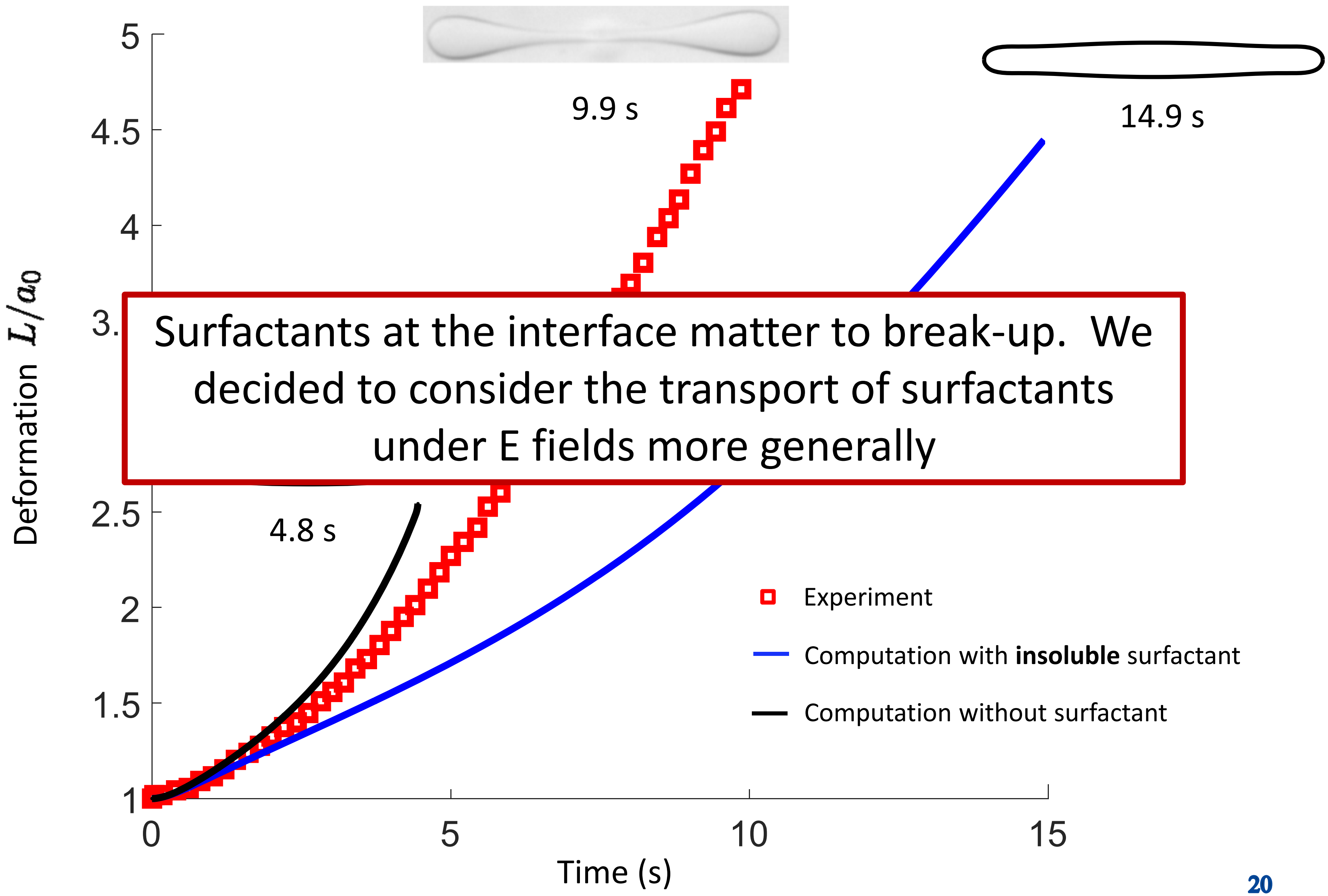
Computations capture experimentally observed breakup mode

Lanauze et al., Soft Matter, 2018

Surfactant addition changes conductivity and interfacial tension



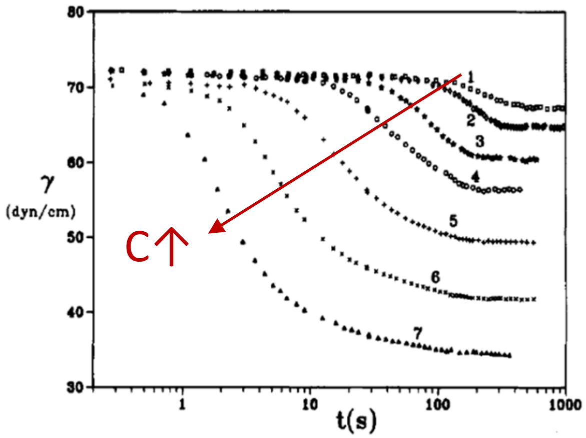
Marangoni stresses change breakup mode



Surfactants at the interface matter to break-up. We decided to consider the transport of surfactants under E fields more generally

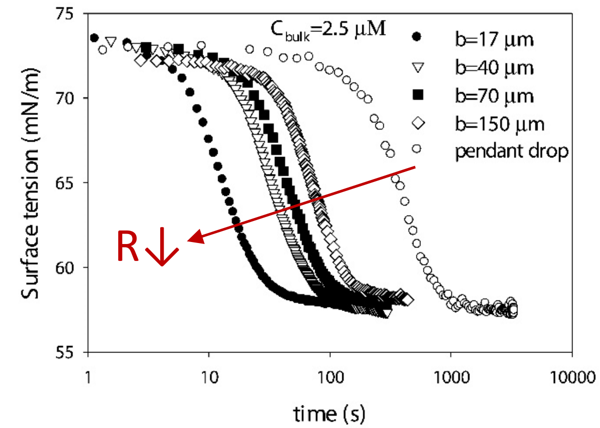
Do electric fields affect surfactant transport?

Bulk concentration



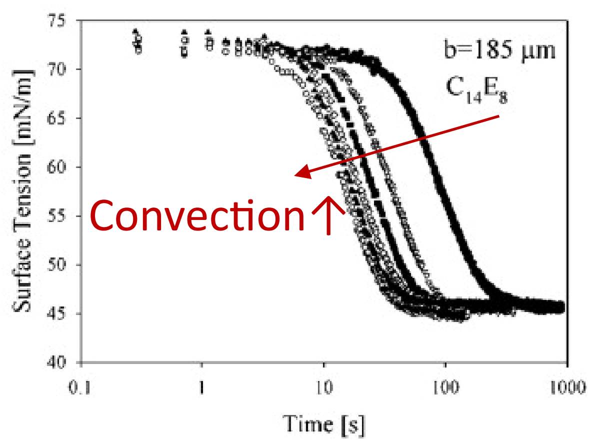
Lin *et al.* (1995)

Interface radius



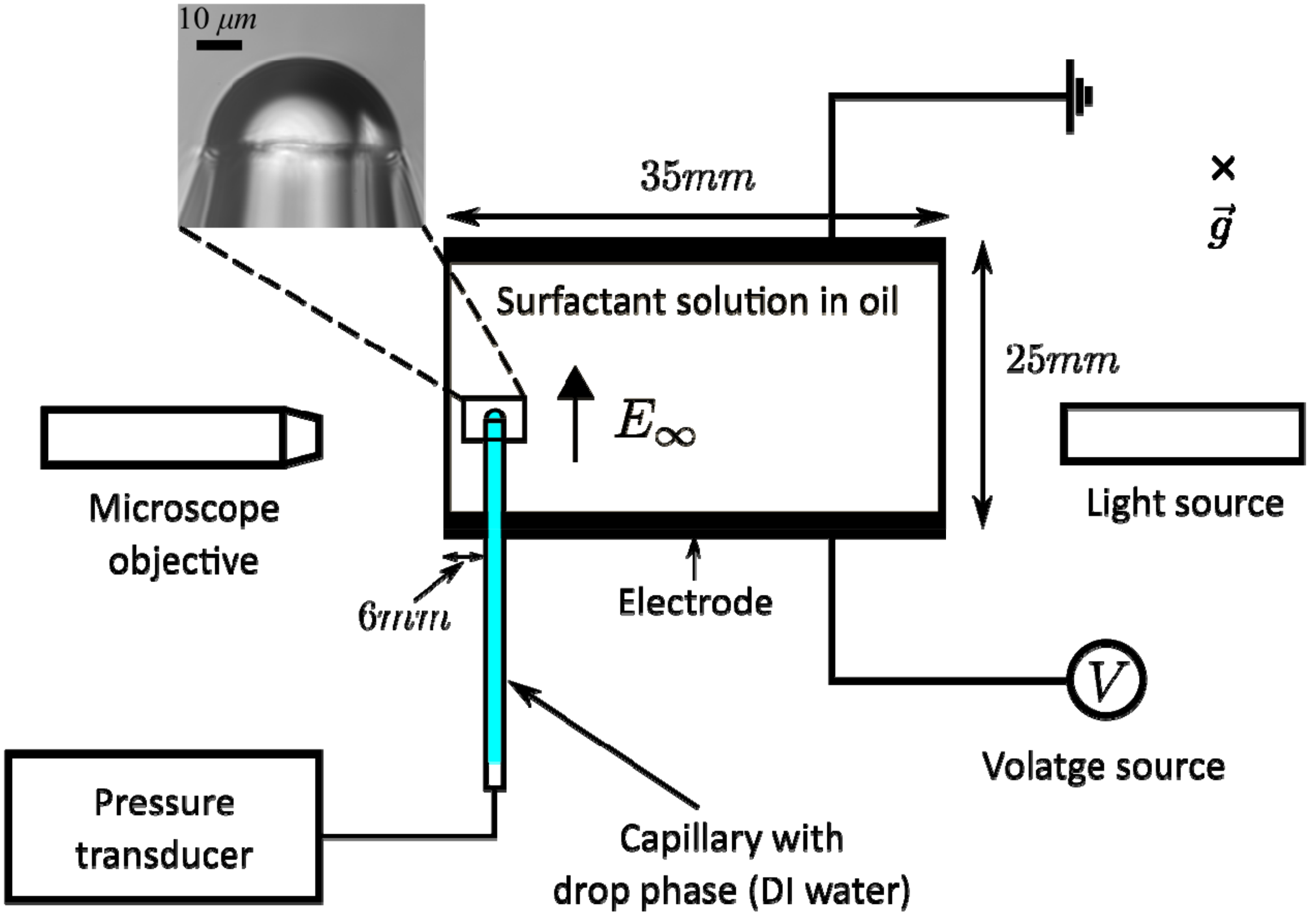
Alvarez *et al.* (2010)

Bulk convection



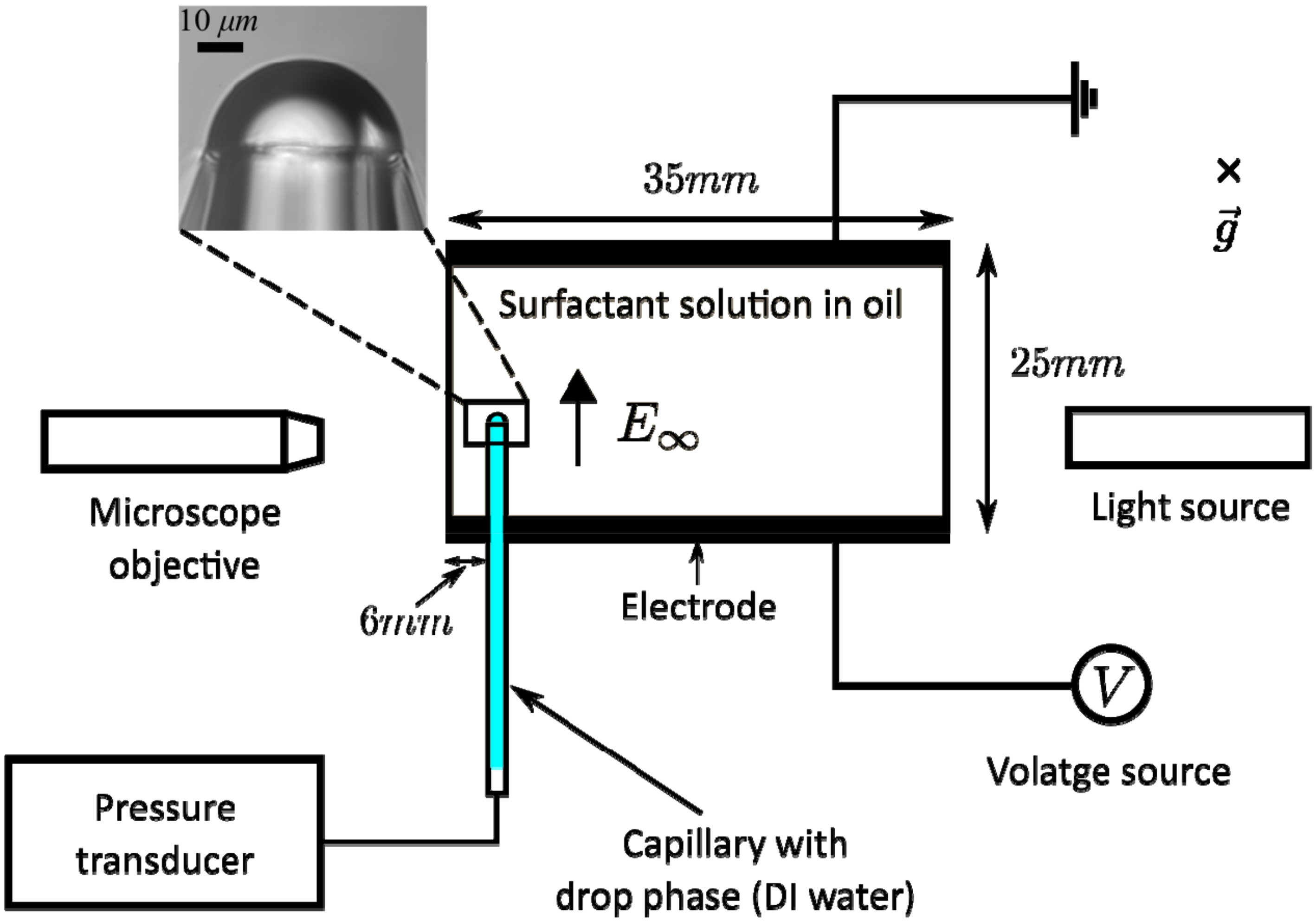
Alvarez *et al.* (2012)

Electrified micro-tensiometer to measure interfacial tension



$$\Delta P = \frac{2\gamma}{R} + \Delta T'_E$$

Electrified micro-tensiometer to measure interfacial tension



$$Ca_E = \frac{R\varepsilon_o E_\infty^2}{\gamma} < 10^{-4}$$

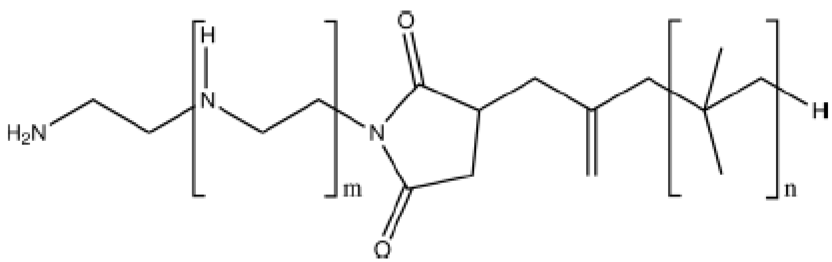
$$\frac{R\Delta P}{\gamma} = 2 + Ca_E \Delta T_E$$

Reservoir phase: Surfactant dispersed in oil

Material 1

Surfactant: Polyisobutylene succinimide

OLOA 11000

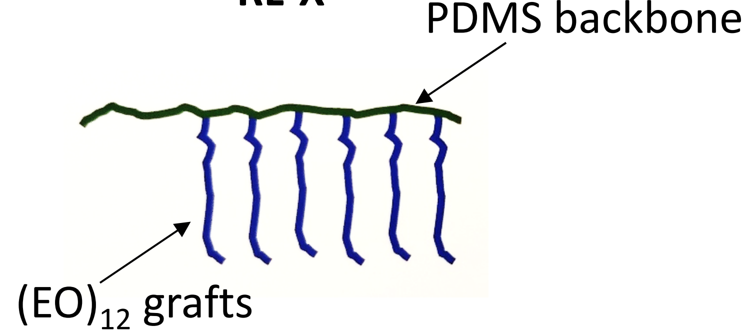


Oil: Isopar-M (alkane mixture)

Material 2

Surfactant: Polydimethylsiloxane (PDMS) based rake surfactant

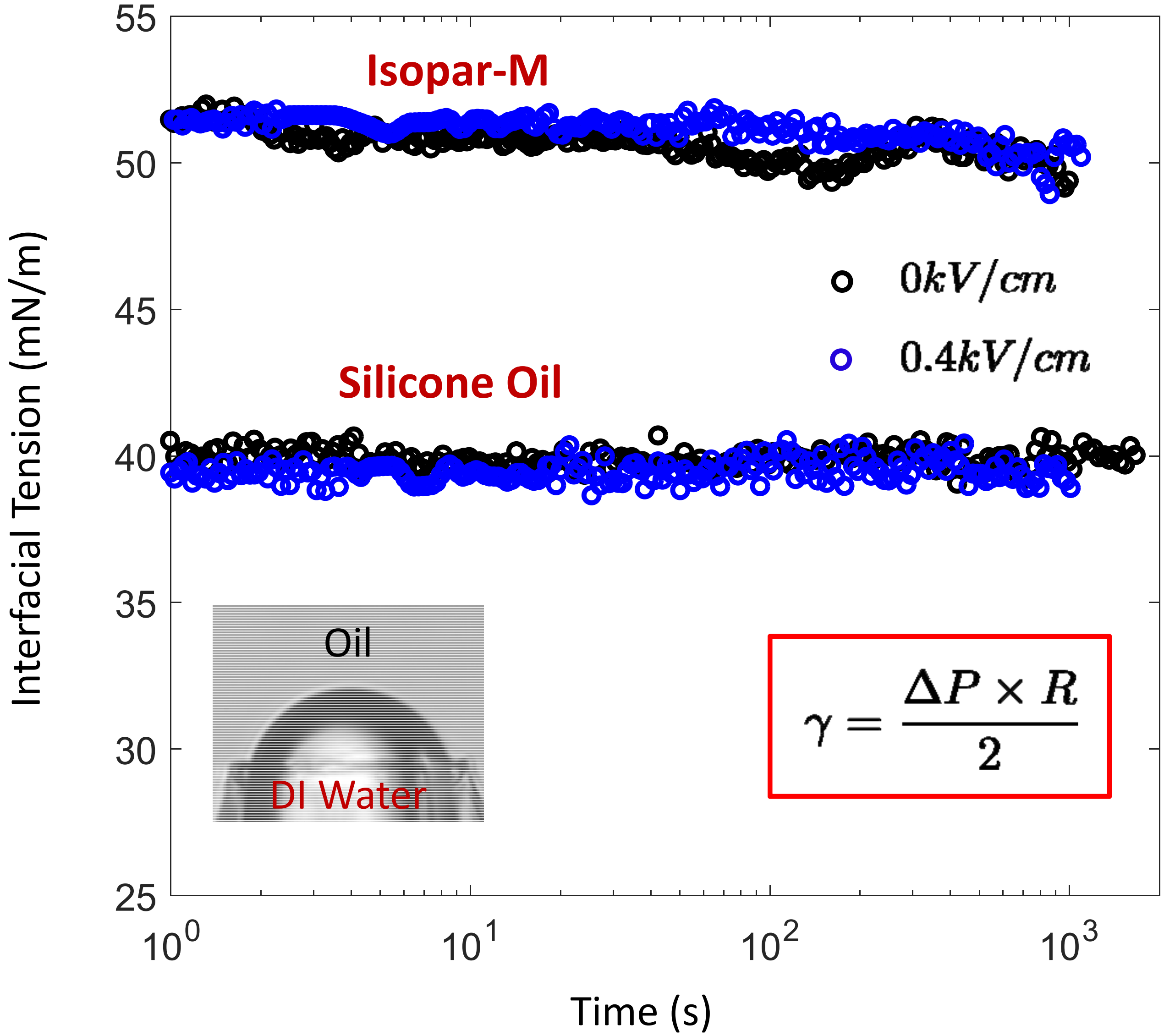
RL-X



Oil: Isopar-M (alkane mixture)

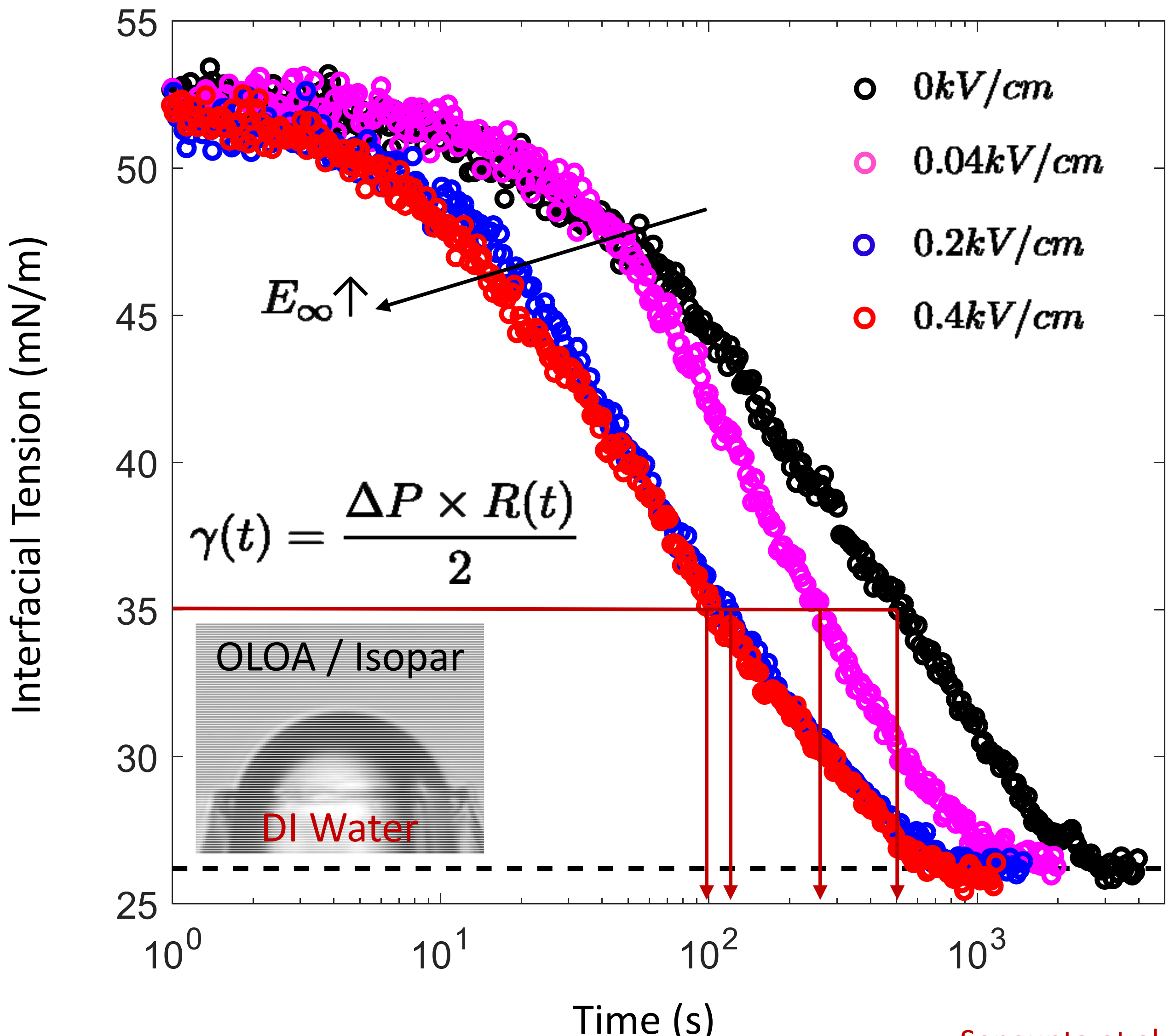
The surfactants ***do not dissociate*** in oil

Electric field does not change interfacial tension of pure oil-water



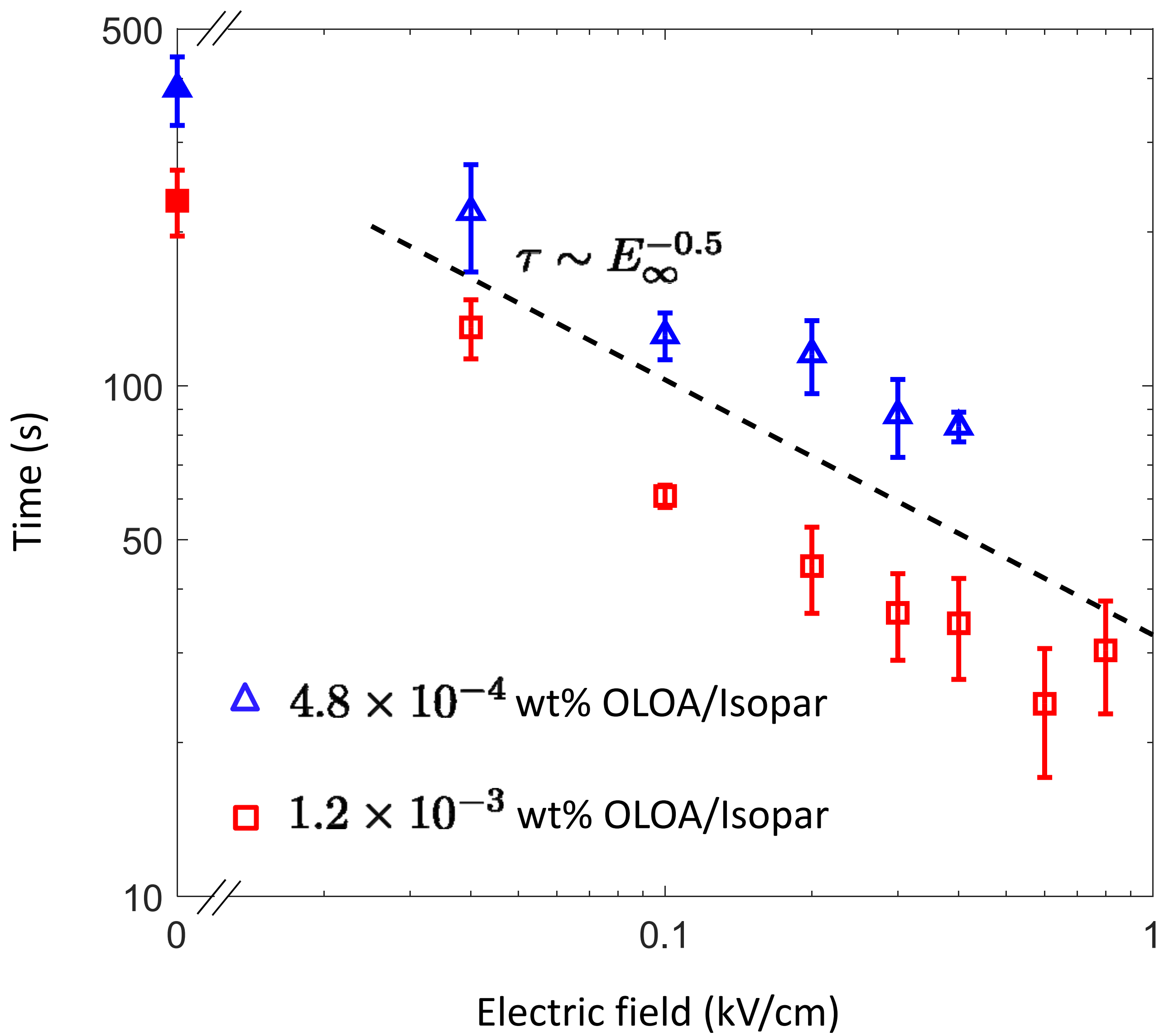
Transport of OLOA is enhanced under electric field

4.8×10^{-4} wt % OLOA 11000 in Isopar

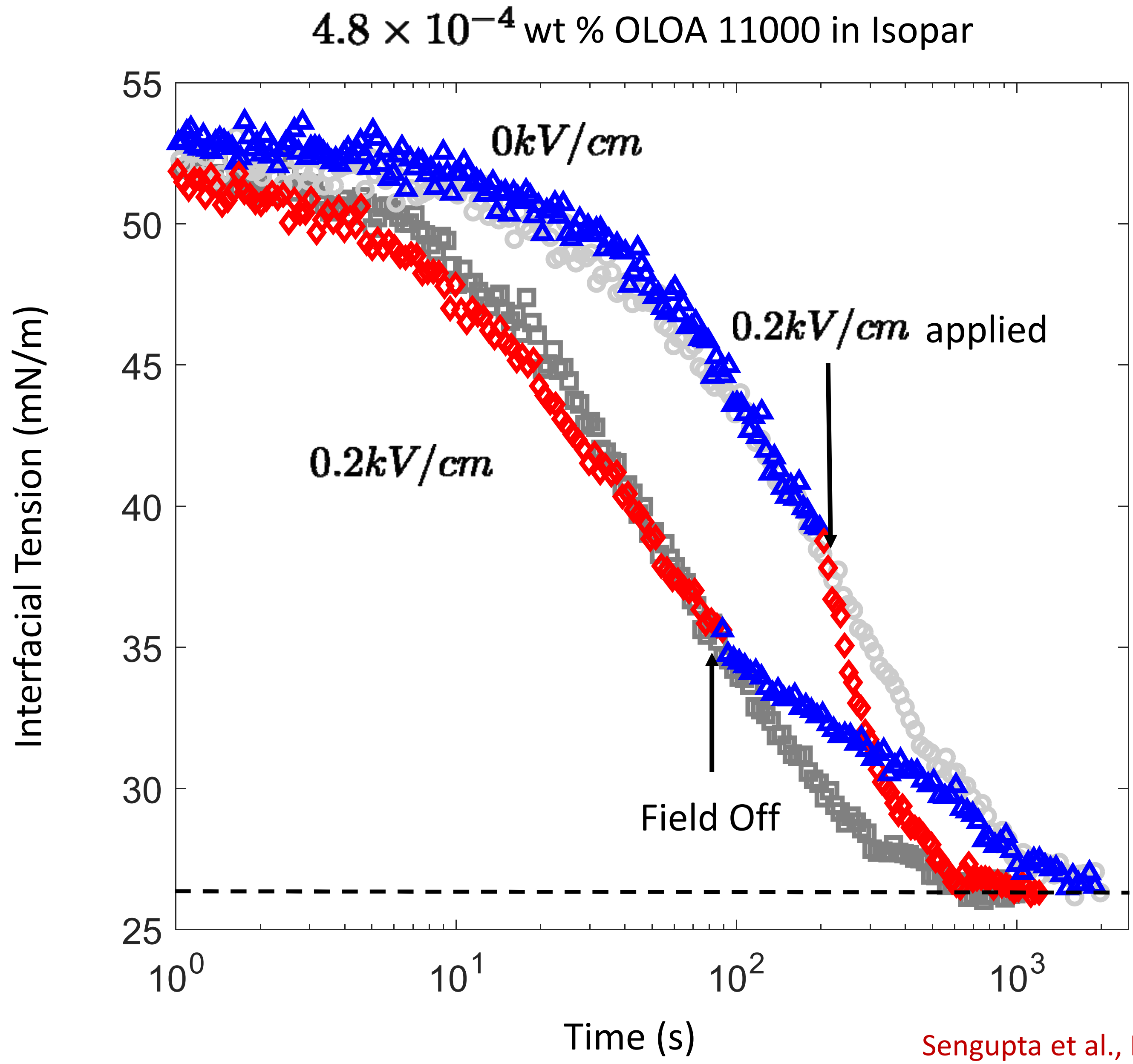


Sengupta et al., PRE, 2019

Time to reach specific interfacial tension decreases with field

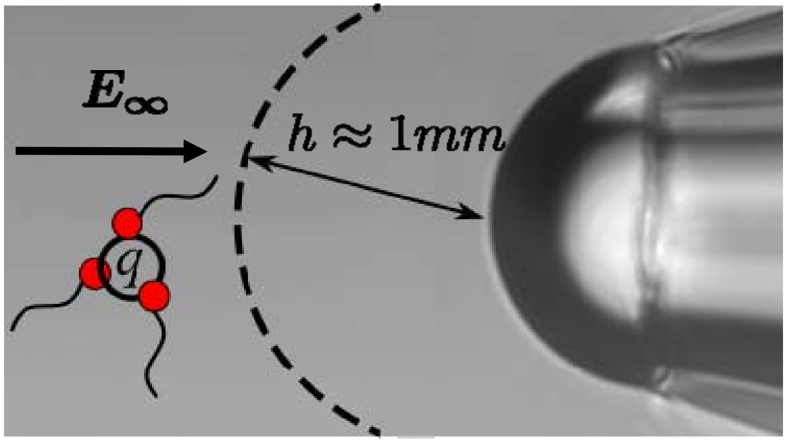


Transport can be precisely controlled by scheduling the field



Sengupta et al., PRE, 2019

Electro-migration of charge carriers result in enhanced transport



Time Scales

Diffusion time scale, $\tau_d = \dfrac{h^2}{D}$ Electrophoretic time scale, $\tau_E = \dfrac{h}{m\, qE_\infty}$

Dimensionless Group

Peclet No, $Pe_E = \dfrac{qhE_\infty}{k_B T} \sim 50 - 5000$

Stokes-Einstein: $D = mk_B T$

Alvarez et al., PRE, 2010
Sengupta et al., PRE 2019

Conclusions

- Unstable suspensions yield accelerated, non-homogeneous breakup

Stable

Unstable

- Electro-migration of surfactant induced charge carriers result in ***precisely controlled, enhanced transport*** under electric fields

Acknowledgements

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- John E. Swearingen Fellowship, Carnegie Mellon University