Basic physics of drops/emulsions, in relation to applications in EOR, cosmetics, foods etc

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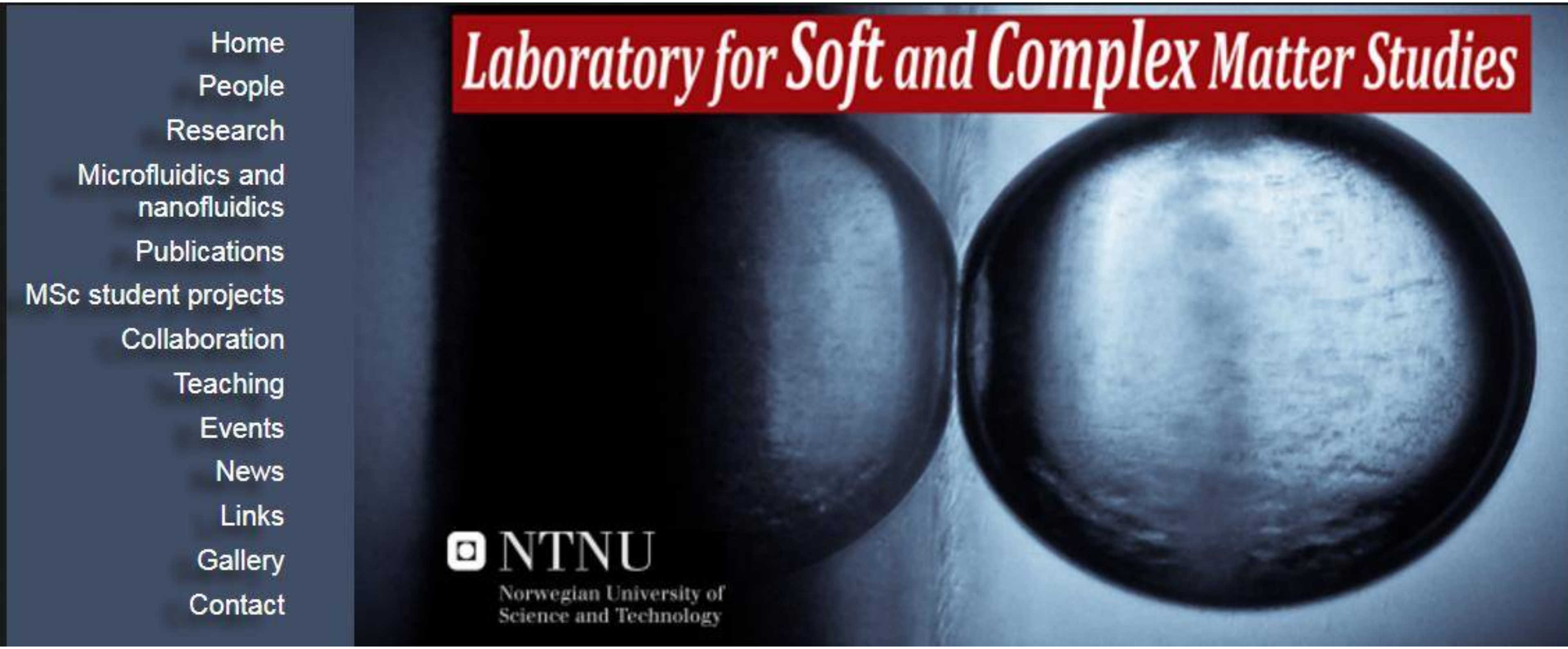

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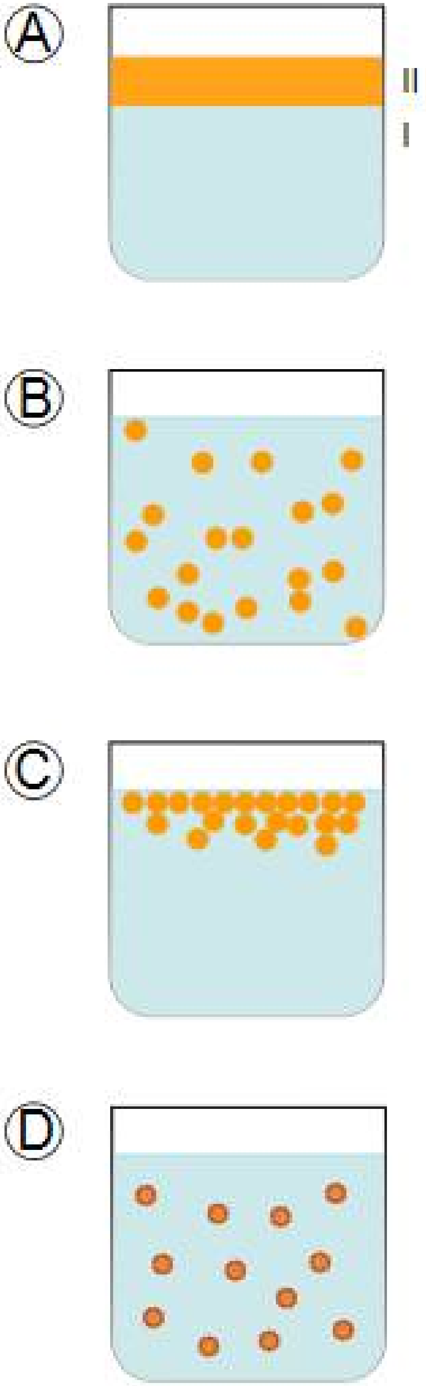
Emulsions (= Systems of MANY drops) are important in many every day and industrial contexts such as:

- in **foods**,
- in the **paint, dyeing and tanning industries**,
- in the manufacture of **synthetic rubber and plastics**,
- in the preparation of **cosmetics** such as shampoos,
- in salves and **pharmaceutical products** for drug delivery,
- in the **petroleum industry** for certain drilling muds, for enhanced oil recovery, in oil refining and oil separation (de-emulsification) and oil&gas transport.

«Classical» («chemical») emulsions

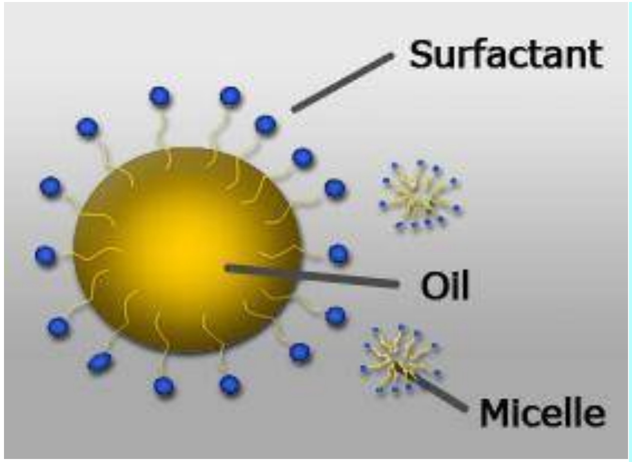


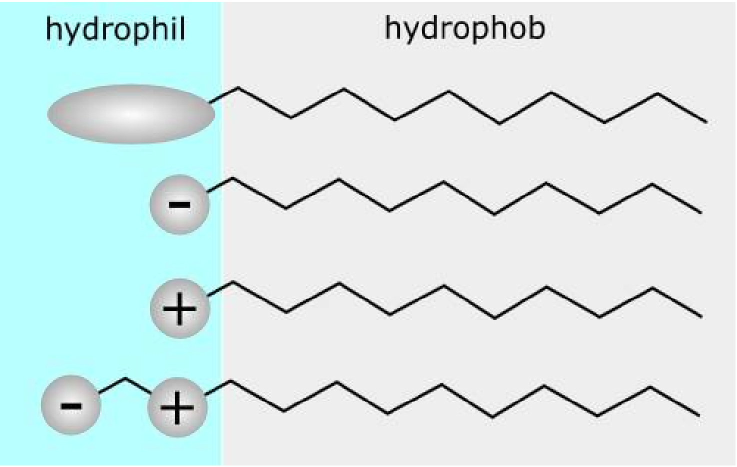
Legend

🟦 Phase I
🟧 Phase II
🟪 Surfactant

A. Two immiscible liquids, not emulsified
B. Emulsion of Phase II dispersed in Phase I
C. The unstable emulsion progressively separates
D. Surfactant positions itself on interface between Phases I and II, stabilizing emulsion

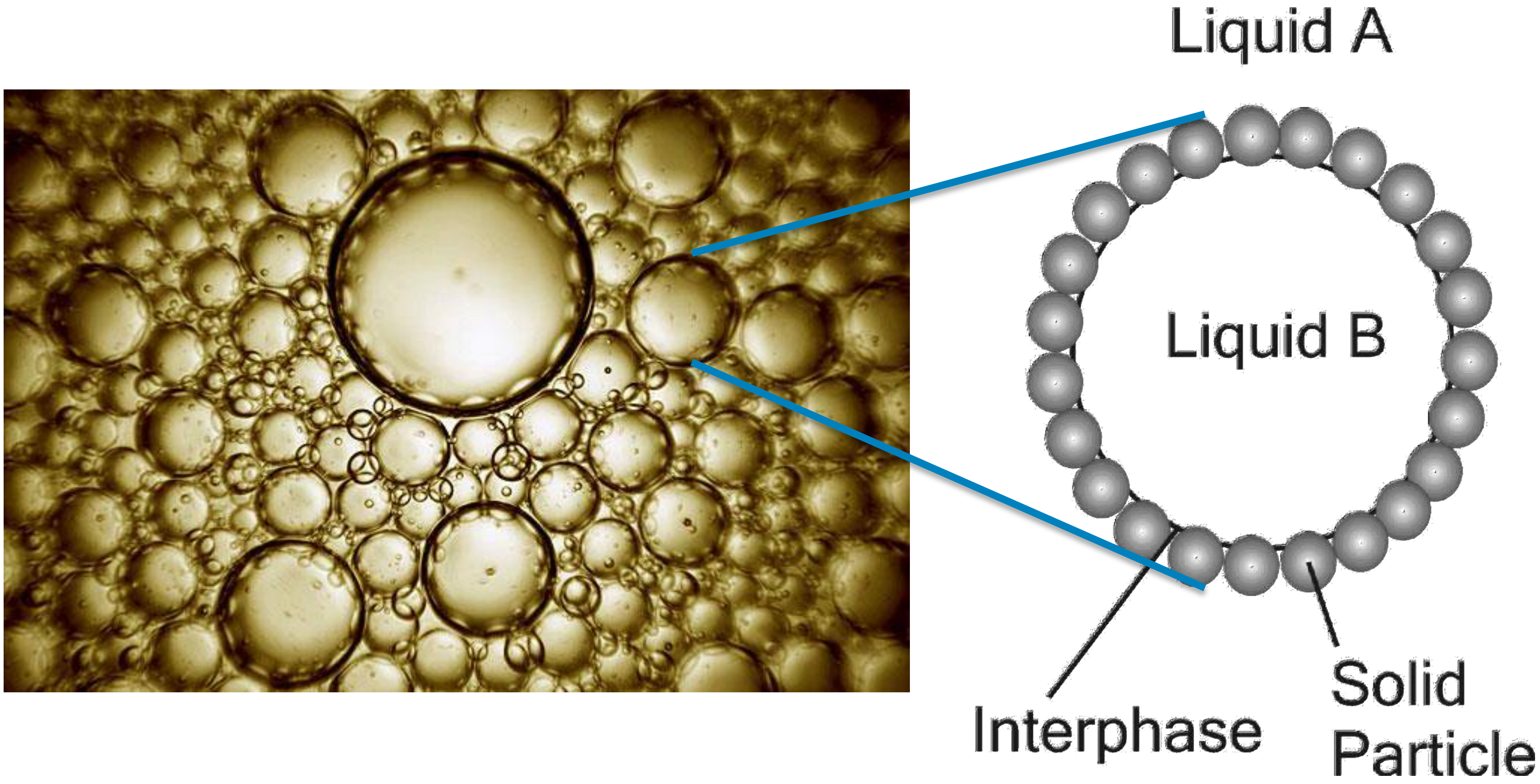
$E_{bind} > \sim k_B T$



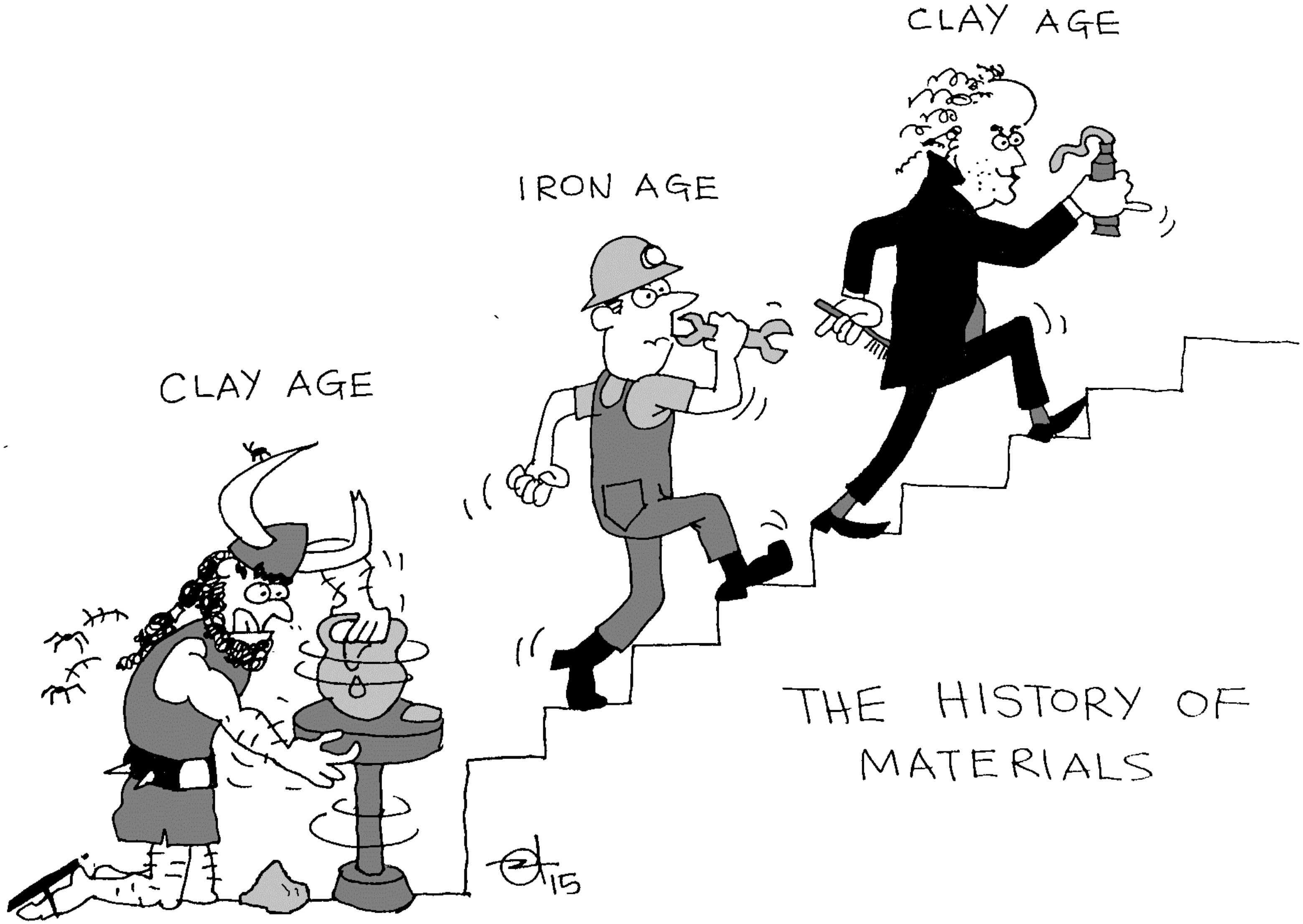


«Classical» («chemical») emulsions

Colloidal particles as emulsion stabilizers: Pickering («physical») emulsions



Pickering («physical») emulsions



Drawing by Ernesto Altshuler

Oil drops in saline water with suspended Laponite clay particles: Pickering emulsion

Article | OPEN

Transition from glass- to gel-like states in clay at a liquid interface

A. Gholamipour-Shirazi, M. S. Carvalho, M. F. G. Huila, K. Araki, P. Dommersnes & J. O. Fossum

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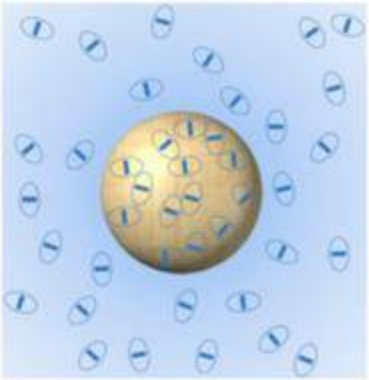
Controlled microfluidic emulsification of oil in a clay nanofluid: Role of salt for Pickering stabilization

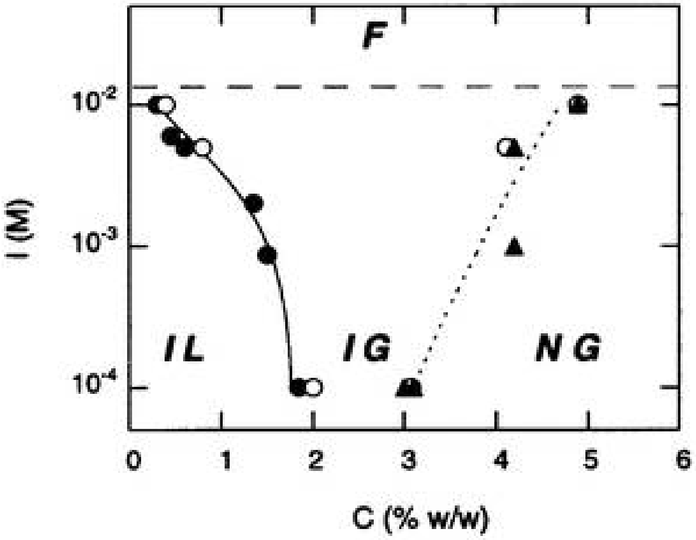
Authors | Authors and affiliations

A. Gholamipour Shirazi, M.S. Carvalho, J.O. Fossum



No salt:
Pickering film
not observable by
Raman microscopy.
Observable surface tension.

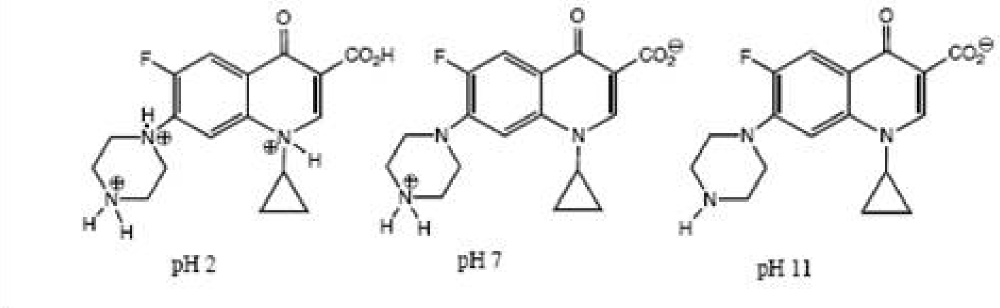
With salt:
~ 4 μm Pickering film.
Increased surface tension.



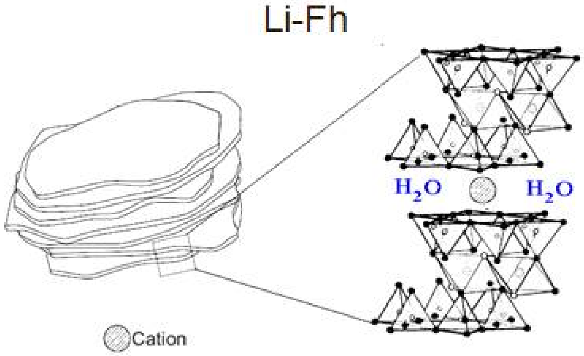
Cipro (ciprofloxacin) is an antibiotic in a group of drugs called fluoroquinolones (flor-o-KWIN-o-lones). It is used to fight bacteria in the body. Cipro is used to treat different types of bacterial infections. It may also be used to prevent or slow anthrax after exposure.

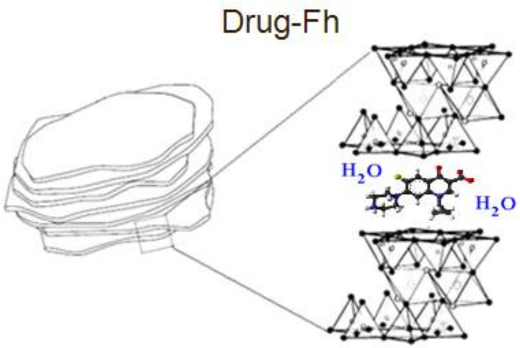
$C_{17}H_{18}FN_3O_3$

Zwitterionic



Positive **Dipole** **Negative**





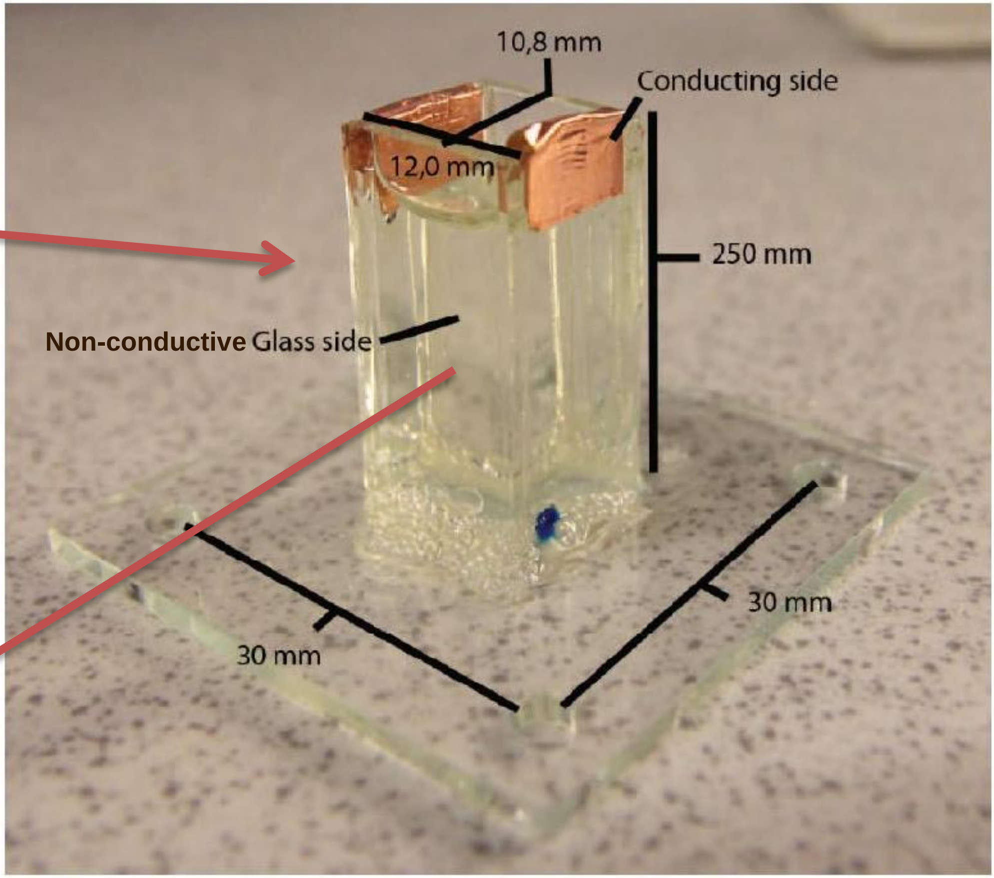
Intercalates by far best for acid pH

Different intercalation mechanism at pH 7?

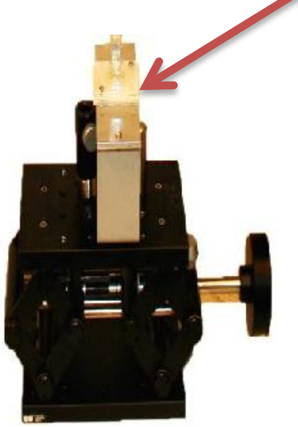
Rapid release at basic pH

Techniques: XRD, UV-VIS Spectroscopy

Sample cell



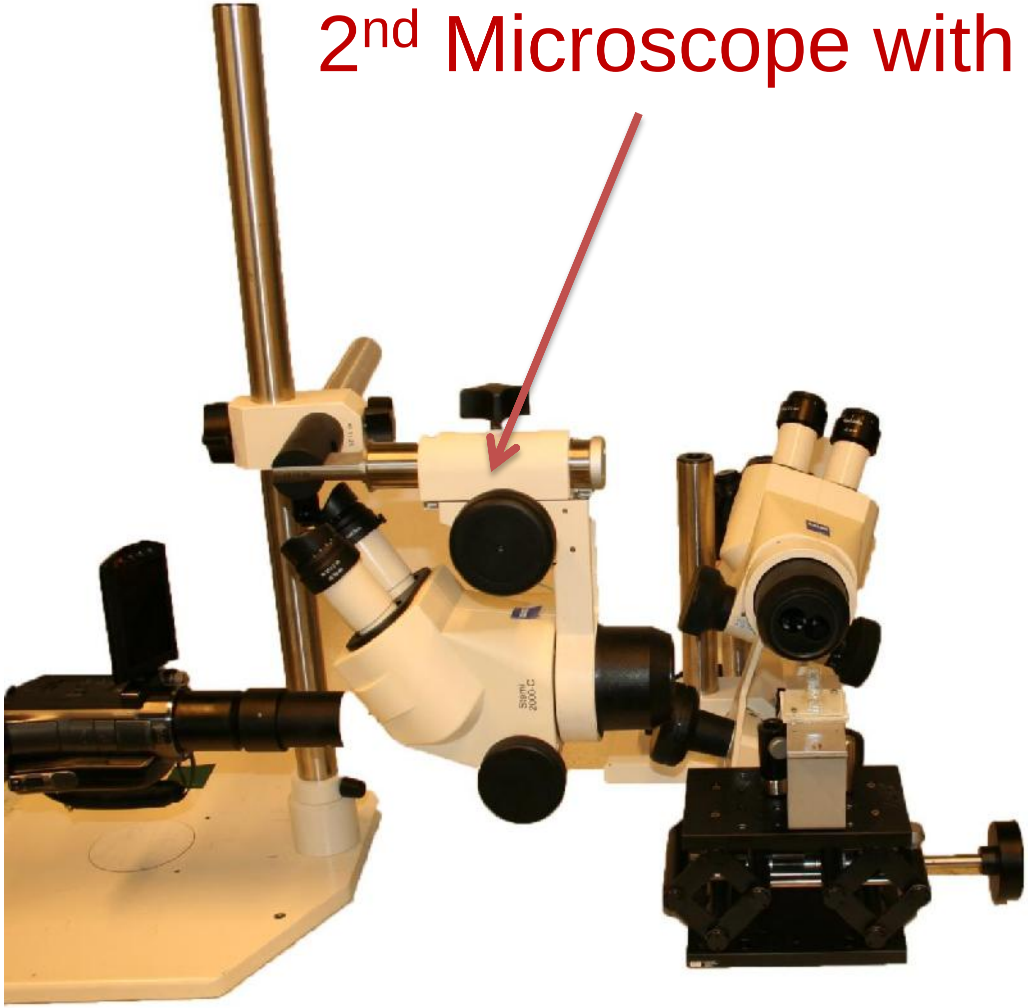
Translation stages



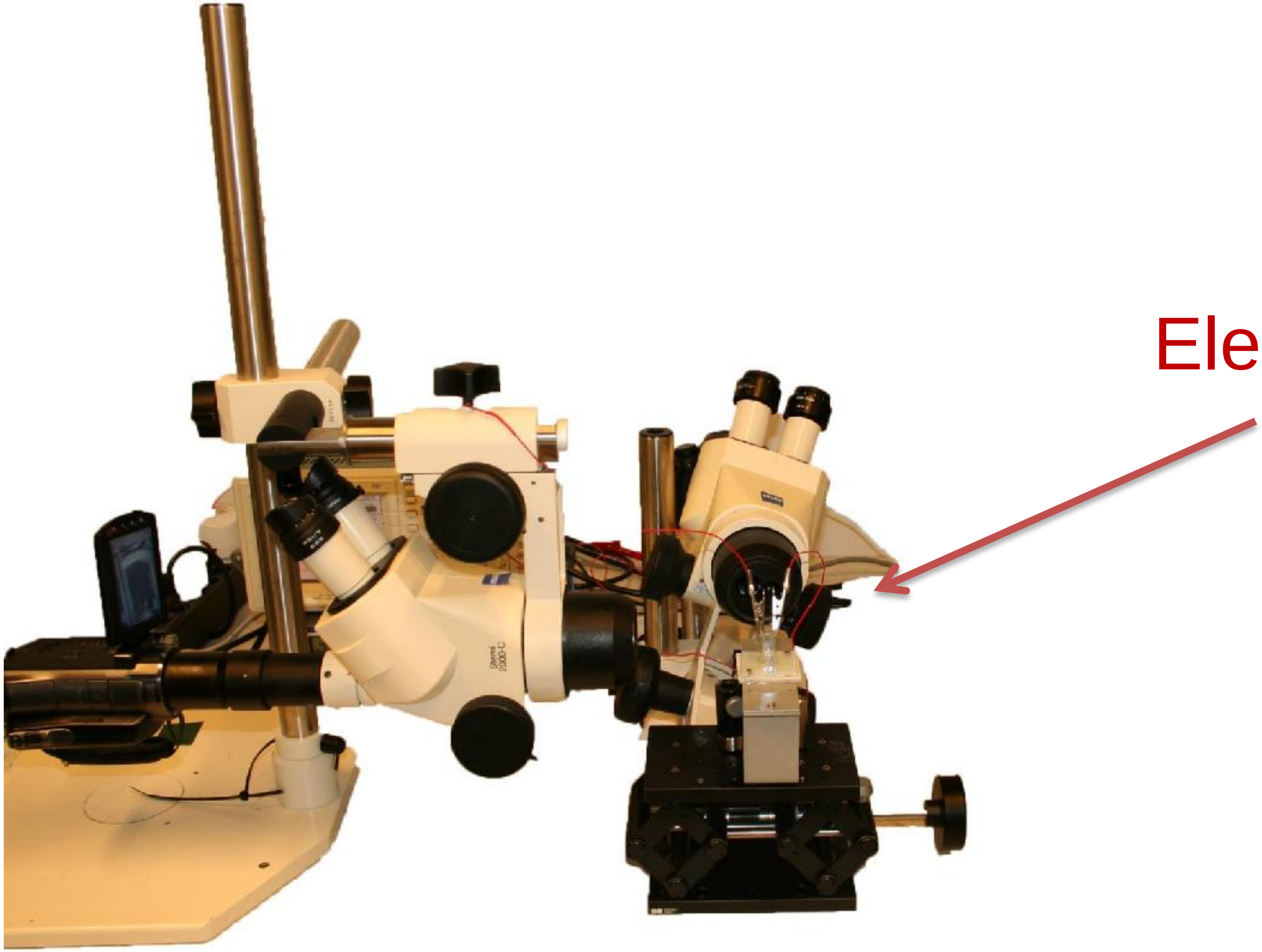
Experimental setup at NTNU Trondheim

1^{st} Microscope with camera

2nd Microscope with camera

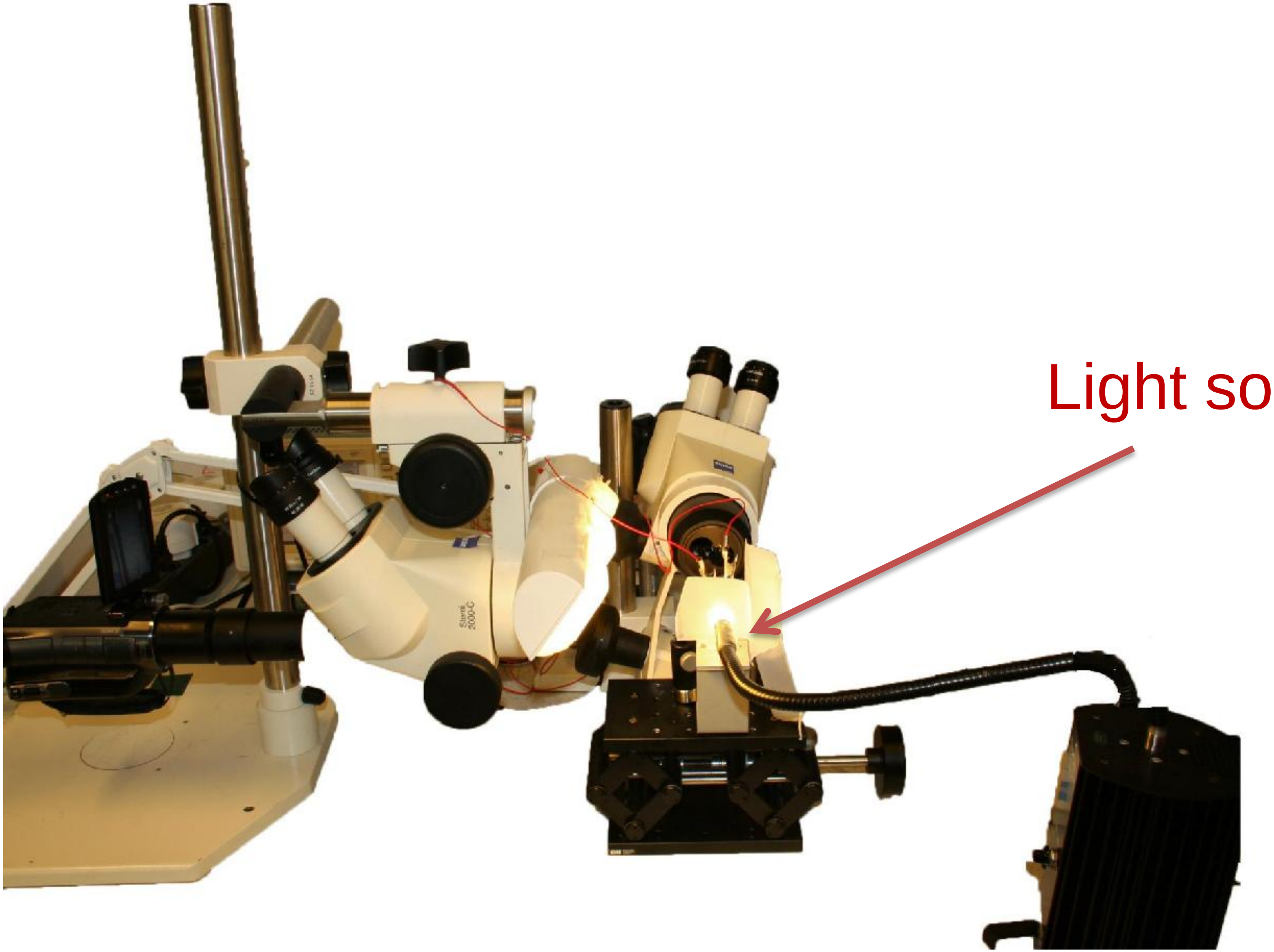


Experimental setup at NTNU Trondheim

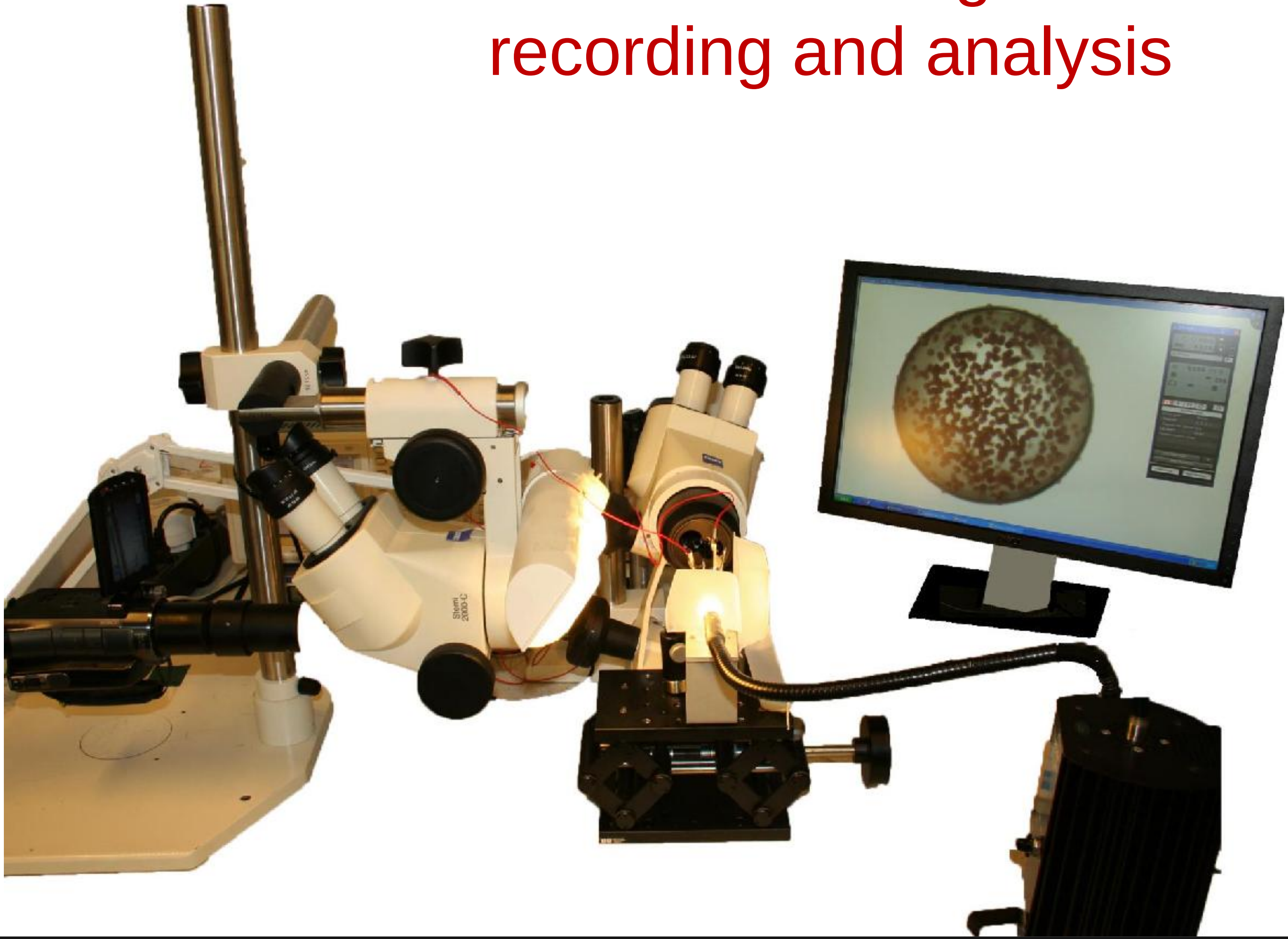


Electrodes

Experimental setup at NTNU Trondheim



Experimental setup at NTNU Trondheim



PC for image
recording and analysis

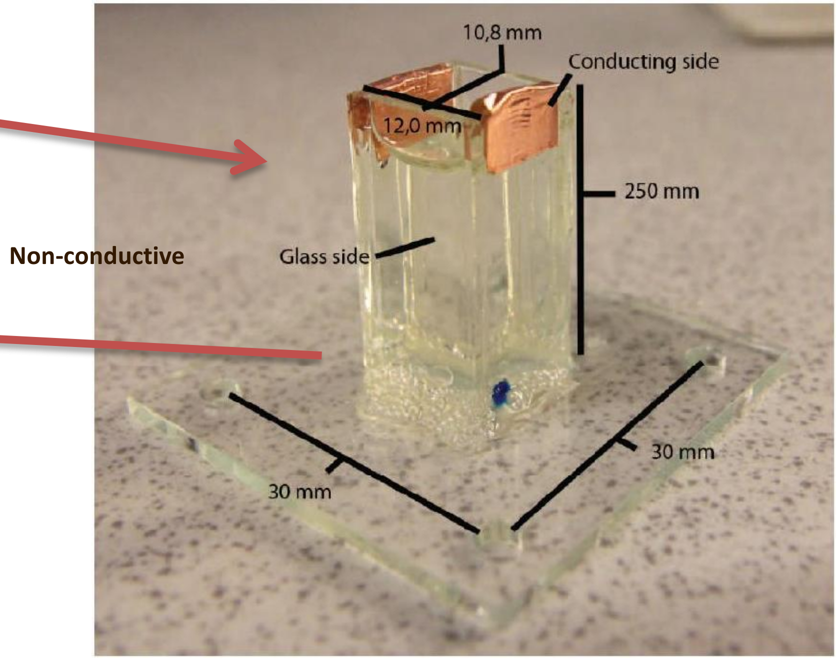
Experimental setup at NTNU Trondheim

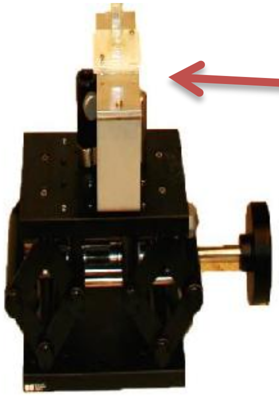
What did we see under the microscope?

Sample cell

2x ITO transparent electrodes

2x glass walls





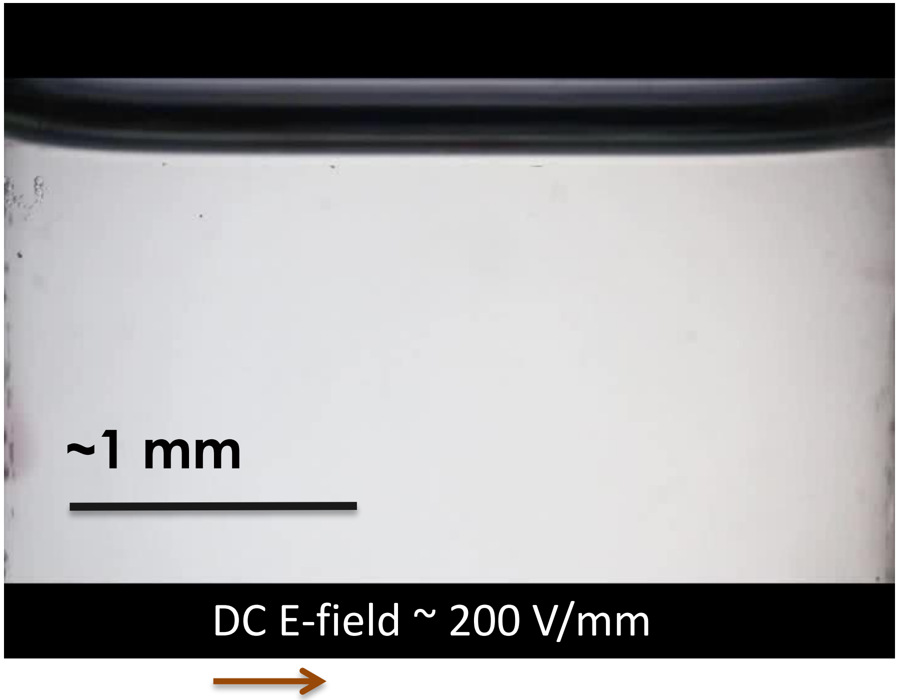
Translation stages

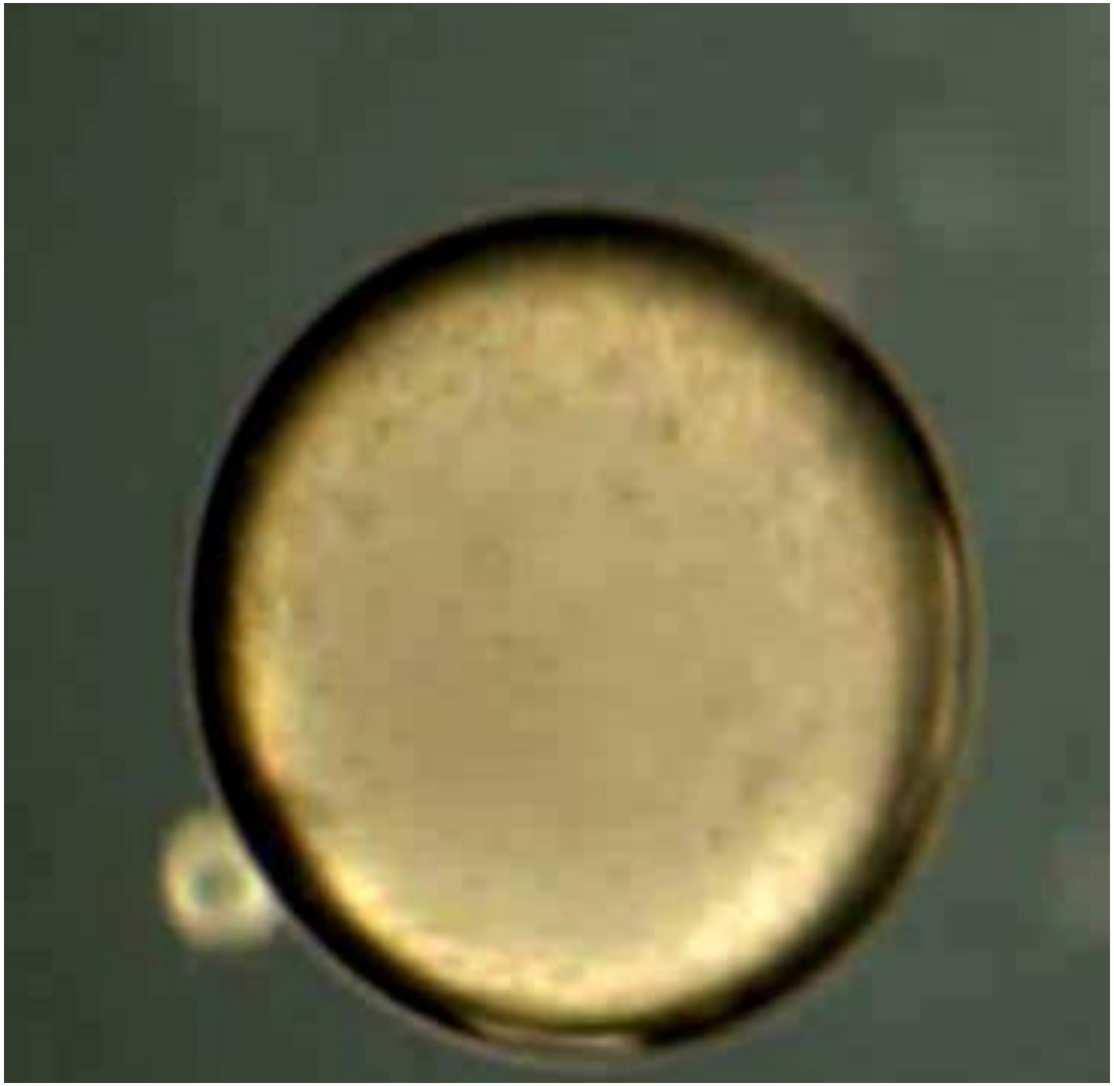
Clay in silicone oil dispersion

(~ 1 mm diameter drop)

Castor oil

(continuous phase)



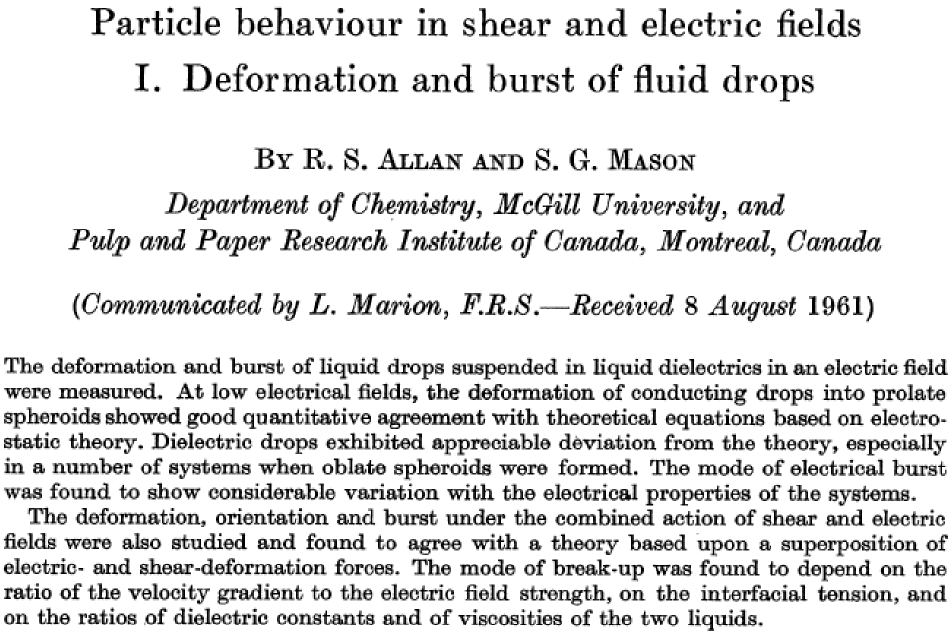


Speeded up x10

E-field induces flows of liquids

Described as "*one of the most notable scientists of the 20th century*"

Sir Geoffrey Ingram Taylor (1886-1975)



Particle behaviour in shear and electric fields

I. Deformation and burst of fluid drops

BY R. S. ALLAN AND S. G. MASON

Department of Chemistry, McGill University, and
Pulp and Paper Research Institute of Canada, Montreal, Canada

(*Communicated by L. Marion, F.R.S.—Received* 8 *August* 1961)

The deformation and burst of liquid drops suspended in liquid dielectrics in an electric field were measured. At low electrical fields, the deformation of conducting drops into prolate spheroids showed good quantitative agreement with theoretical equations based on electrostatic theory. Dielectric drops exhibited appreciable deviation from the theory, especially in a number of systems when oblate spheroids were formed. The mode of electrical burst was found to show considerable variation with the electrical properties of the systems.

The deformation, orientation and burst under the combined action of shear and electric fields were also studied and found to agree with a theory based upon a superposition of electric- and shear-deformation forces. The mode of break-up was found to depend on the ratio of the velocity gradient to the electric field strength, on the interfacial tension, and on the ratios of dielectric constants and of viscosities of the two liquids.

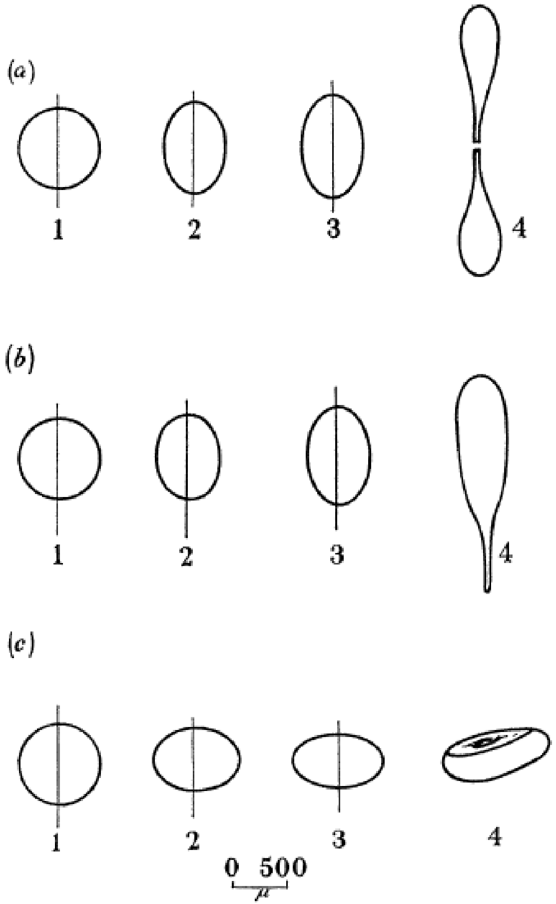


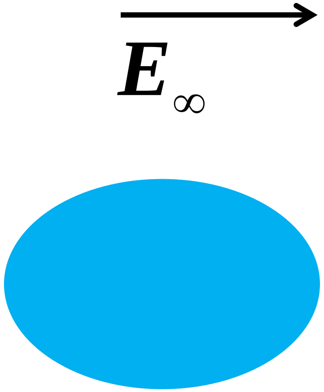
FIGURE 3. Tracings from typical photographs of drops in an electric field showing the change in D_e with increasing E_0 up to break-up. (*a*) $q = \infty$ (system 13). The drop in picture 4 separated into two halves with a large number of fine droplets in between at $(E_0^2 b) = 2{\cdot}9 \times 10^5\,\mathrm{V^2\,cm^{-1}}$. (*b*) $1 < q < \infty$ (system 2). The drops were drawn out into threads starting from the end nearest the negative electrode (as shown) followed by extension of the other end to the positive electrode at $(E_0^2 b) = 5{\cdot}4 \times 10^5\,\mathrm{V^2\,cm^{-1}}$. (*c*) $q < 1$ (system 7). The drops were flattened into a sheet initially in the XZ plane (picture 4), which then folded over until it was no longer co-planar. The flattened drop eventually broke up unevenly at $(E_0^2 b) = 3{\cdot}7 \times 10^6\,\mathrm{V^2\,cm^{-1}}$.

Allan, RS & **Mason**, SG, **1962** Pros. **Roy**. **Soc**. A, **267**, 45—61

Fluid drops subject to a uniform electric DC field

Perfect dielectric drop:

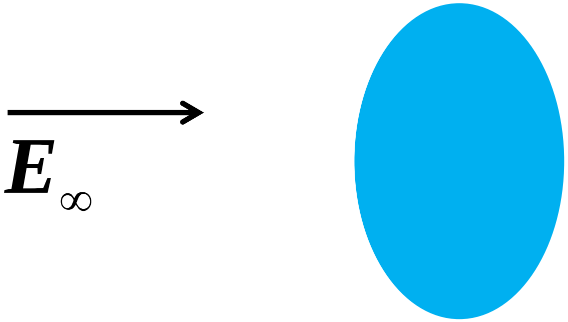
Drop deformation



Prolate shape

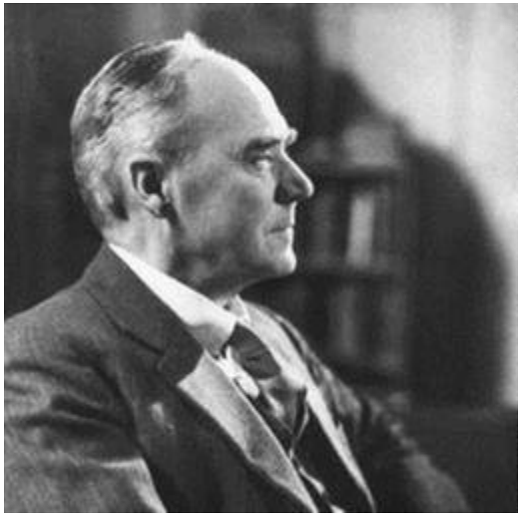
Weakly conducting drop (G. I. Taylor’s insight)::

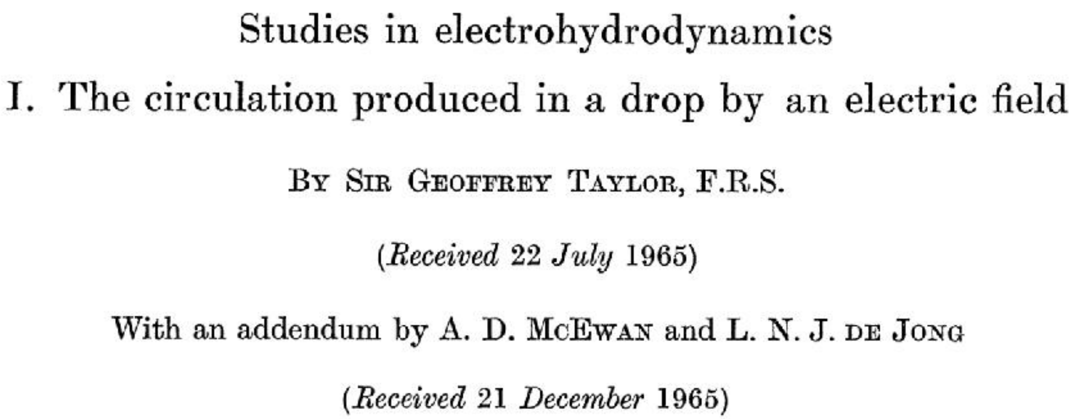
Drop deformation and hydrodynamic flow



Oblate shape

- Conductor fluids: water, mercury
- Dielectric fluids: benzene
- **“Leaky dielectric” fluids:** castor oil, corn oil, mineral oils, etc





Studies in electrohydrodynamics

I. The circulation produced in a drop by an electric field

By Sir Geoffrey Taylor, F.R.S.

(*Received* 22 *July* 1965)

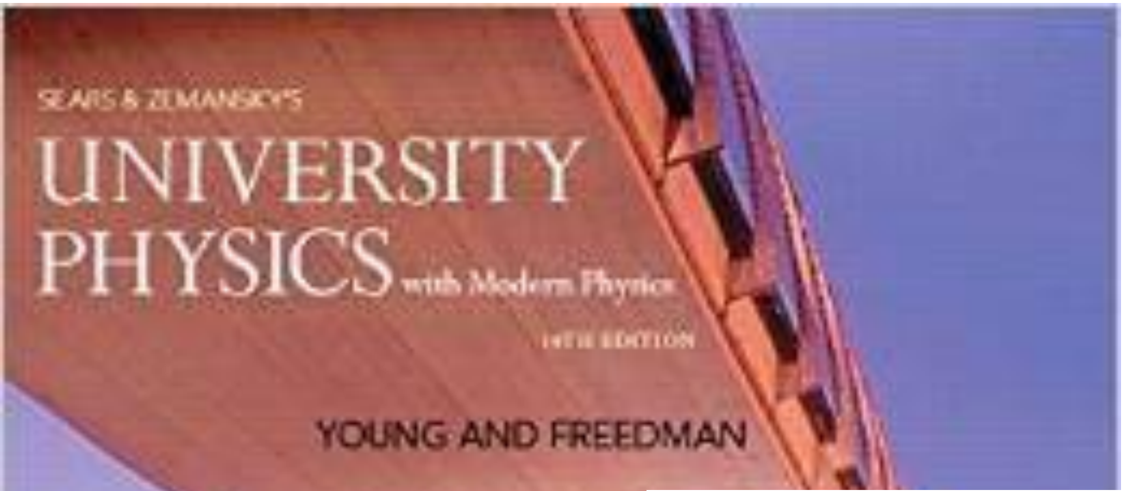
With an addendum by A. D. McEwan and L. N. J. de Jong

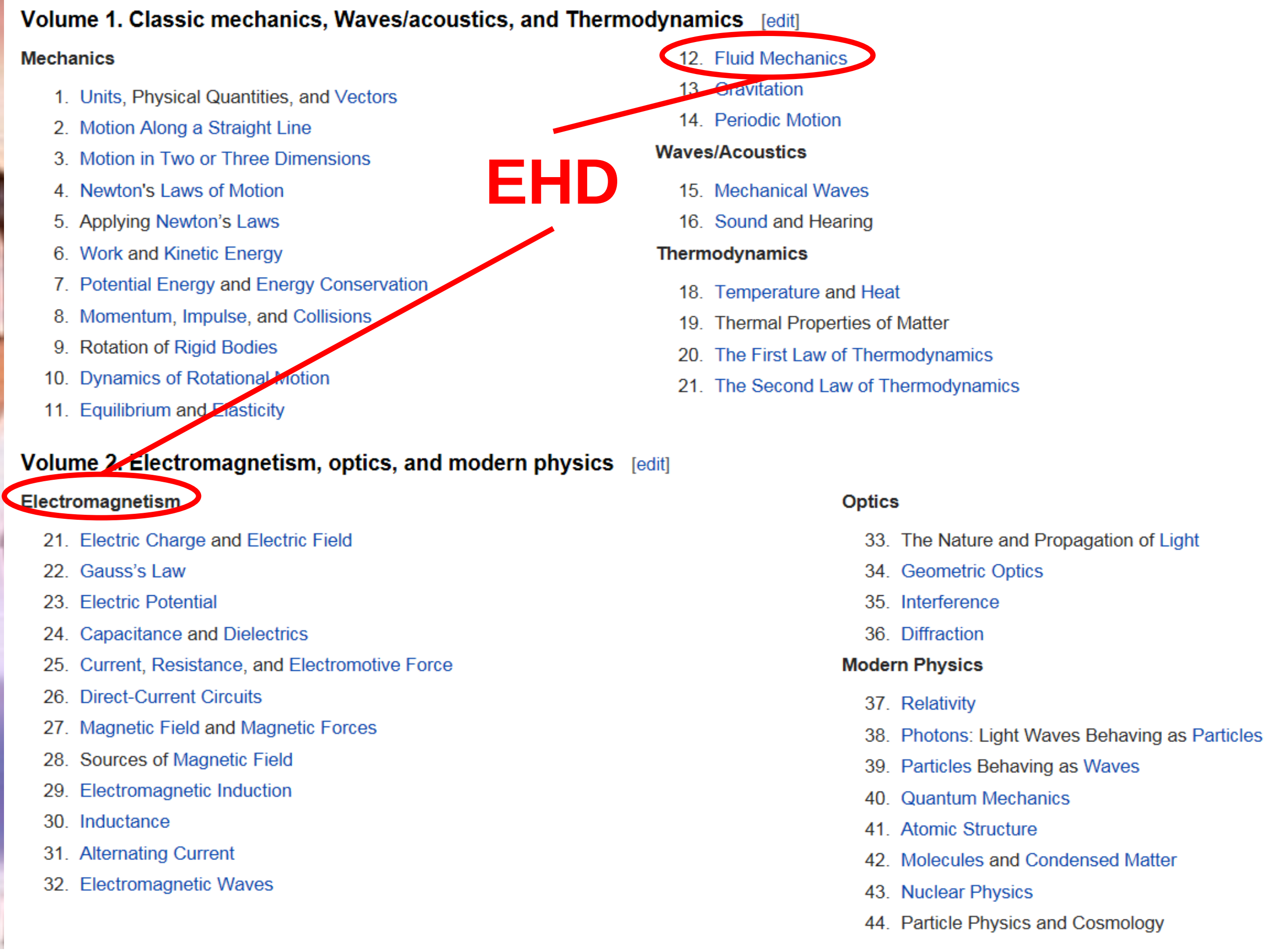
(*Received* 21 *December* 1965)

Proc. R. Soc. Lond. A 291,159-166 (1966)

(see also review by Saville - 1997)

Coupling two undergrad textbook chapters





Volume 1. Classic mechanics, Waves/acoustics, and Thermodynamics [edit]

Mechanics

1. Units, Physical Quantities, and Vectors
2. Motion Along a Straight Line
3. Motion in Two or Three Dimensions
4. Newton's Laws of Motion
5. Applying Newton's Laws
6. Work and Kinetic Energy
7. Potential Energy and Energy Conservation
8. Momentum, Impulse, and Collisions
9. Rotation of Rigid Bodies
10. Dynamics of Rotational Motion
11. Equilibrium and Elasticity
12. Fluid Mechanics
13. Gravitation
14. Periodic Motion

Waves/Acoustics

15. Mechanical Waves
16. Sound and Hearing

Thermodynamics

18. Temperature and Heat
19. Thermal Properties of Matter
20. The First Law of Thermodynamics
21. The Second Law of Thermodynamics

Volume 2. Electromagnetism, optics, and modern physics [edit]

Electromagnetism

21. Electric Charge and Electric Field
22. Gauss's Law
23. Electric Potential
24. Capacitance and Dielectrics
25. Current, Resistance, and Electromotive Force
26. Direct-Current Circuits
27. Magnetic Field and Magnetic Forces
28. Sources of Magnetic Field
29. Electromagnetic Induction
30. Inductance
31. Alternating Current
32. Electromagnetic Waves

Optics

33. The Nature and Propagation of Light
34. Geometric Optics
35. Interference
36. Diffraction

Modern Physics

37. Relativity
38. Photons: Light Waves Behaving as Particles
39. Particles Behaving as Waves
40. Quantum Mechanics
41. Atomic Structure
42. Molecules and Condensed Matter
43. Nuclear Physics
44. Particle Physics and Cosmology

Maxwell-Wagner charge relaxation time

Ohmic conductor:

$$\boldsymbol{J} = \sigma \boldsymbol{E}$$

Maxwell (Gauss) equation:

$$\nabla \cdot \varepsilon \boldsymbol{E} = \rho_f$$

Charge conservation:

$$\frac{\partial \rho_f}{\partial t} + \nabla \cdot \boldsymbol{J} = 0$$

Exponential decay of free charges in bulk:

$$\frac{\partial \rho_f}{\partial t} + \frac{1}{\tau_{MW}} \rho_f = 0$$

$$\rho_f \propto e^{-t/\tau_{MW}}$$

$$\tau_{MW} = \frac{\varepsilon}{\sigma}$$

Time it takes to reach electrical stationary state

Maxwell-Wagner time

Keep free charges

Conducting fluids

Maxwell-Wagner charge relaxation time: Example

Castor oil:

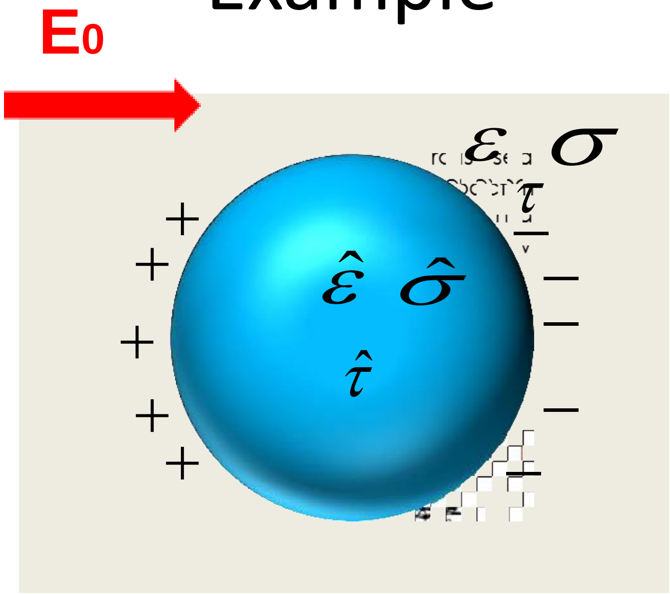
$$\sigma = 45\, pS/m$$

$$\varepsilon = 4.7\varepsilon_0$$

Silicon oil:

$$\hat{\sigma} = 4\, pS/m$$

$$\hat{\varepsilon} = 2.1\varepsilon_0$$



Combined MW time: $\tau_{MW} = \dfrac{2\varepsilon + \hat{\varepsilon}}{2\sigma + \hat{\sigma}} \approx 1\sec$

After about 1 second there are no free charges in bulk, only at boundaries

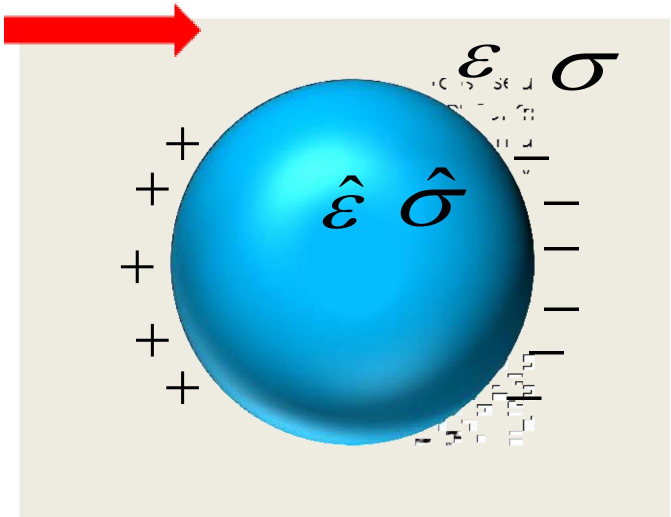
Conducting fluids

$$\nabla \cdot \varepsilon \vec{E} = \rho_f$$

$$\sigma E_n = \hat{\sigma} \hat{E}_n$$

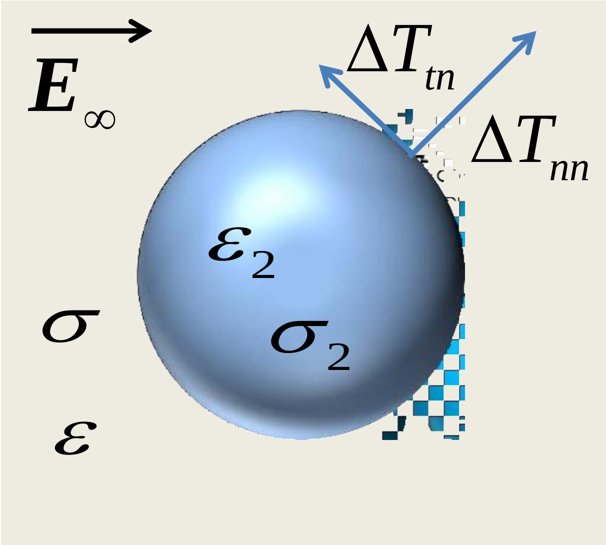
$$\varepsilon E_n - \hat{\varepsilon} \hat{E}_n = \rho_f$$

$$E_t = \hat{E}_t$$



Free charges on the droplet surface:

$$\sigma_f = 3E \frac{\sigma \hat{\sigma}}{\sigma + \hat{\sigma}} (\tau - \hat{\tau}) \cos(\theta)$$



$$\mathbf{T} = \varepsilon\left(\vec{E}\vec{E} - \frac{1}{2}E^2\boldsymbol{I}\right)$$

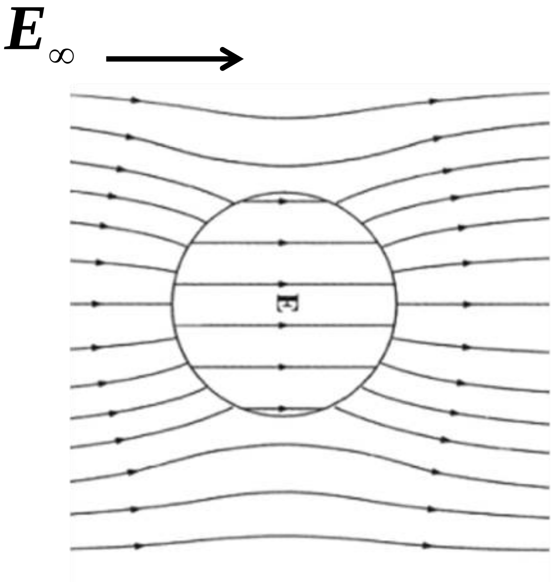
$$\Delta T_{tn} = (\varepsilon_1 E_{1n} - \varepsilon_2 E_{2n})E_t = \sigma_f E_t$$

$$\Delta T_{nn} = \varepsilon_1(E_{1n}{}^2 - \frac{1}{2}E_1{}^2) - \varepsilon_2(E_{2n}{}^2 - \frac{1}{2}E_2{}^2)$$

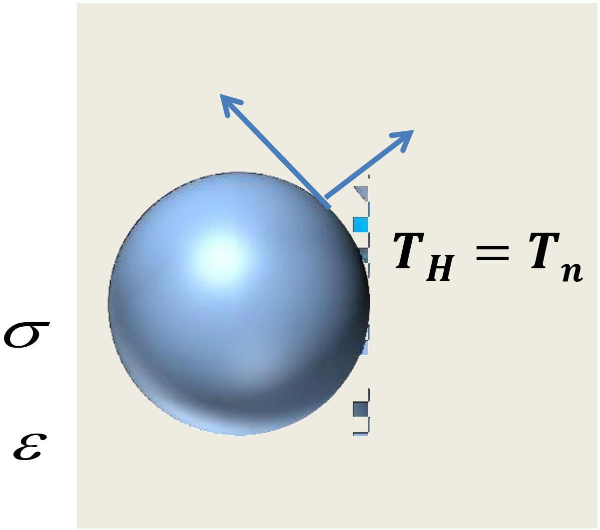
ΔT_{nn} ⇒ Deforms the drop

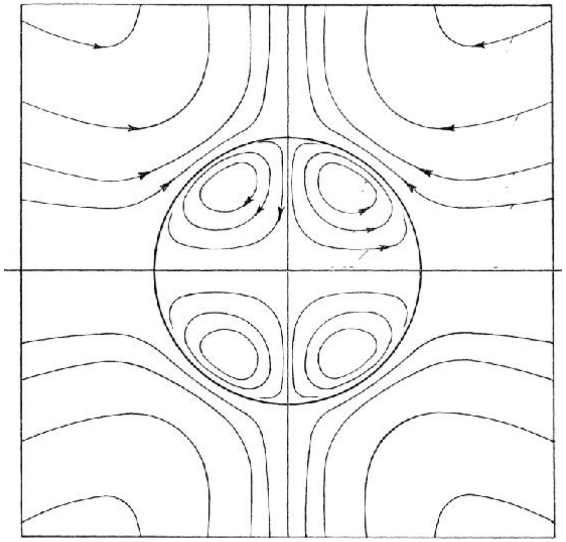
ΔT_{tn} ⇒ Induce fluid flow

Electric forces on the drop surface



Electrostatics





Hydrodynamics

$$\nabla \cdot \varepsilon \vec{E} = \rho_f$$

$$\nabla \times \vec{E} = 0$$

$$\boldsymbol{T_M} = \varepsilon\left(E_i E_j - \frac{1}{2} E^2 \delta_{ij}\right)$$

$$\nabla p = \eta \nabla^2 \vec{v}$$

$$\nabla \cdot \vec{v} = 0$$

$$\boldsymbol{T_H} = -p\delta_{ij} + \eta\left(\frac{\partial v_i}{\partial x_j} + \frac{\partial v_j}{\partial x_i}\right)$$

Electrostatics and hydrodynamics only couple through surface stress balance

Low Reynolds hydrodynamics:

$$\mathrm{Re} = \frac{\text{inertial forces}}{\text{viscous forces}} = \frac{\rho \mathbf{v} L}{\mu} = \frac{\mathbf{v} L}{\nu}$$

Stokes equation $$-\nabla p + \eta \nabla^2 \boldsymbol{v} = 0$$

Standard Stokes hydrodynamics + electric forces at interfaces:

Low Reynolds electro-Hydrodynamics:

Balance of viscous and electric forces: $$-\nabla p + \eta \nabla^2 \boldsymbol{v} + \rho_f \boldsymbol{E} - \frac{1}{2} E^2 \nabla \varepsilon = 0$$

In bulk: $$\nabla \varepsilon = 0$$

At interface: $$\nabla \varepsilon \neq 0 \qquad \rho_f \neq 0$$

Drop

$$\boldsymbol{T}_{Stokes} = \boldsymbol{T}_{Maxwell}$$

$$\mathbf{T}_{Stokes} = -p\mathbf{I} + \eta\left(\nabla \boldsymbol{v} + (\nabla \boldsymbol{v})^T\right) = -p\delta_{ij} + \eta(\nabla v_{ij} + \nabla v_{ji})$$

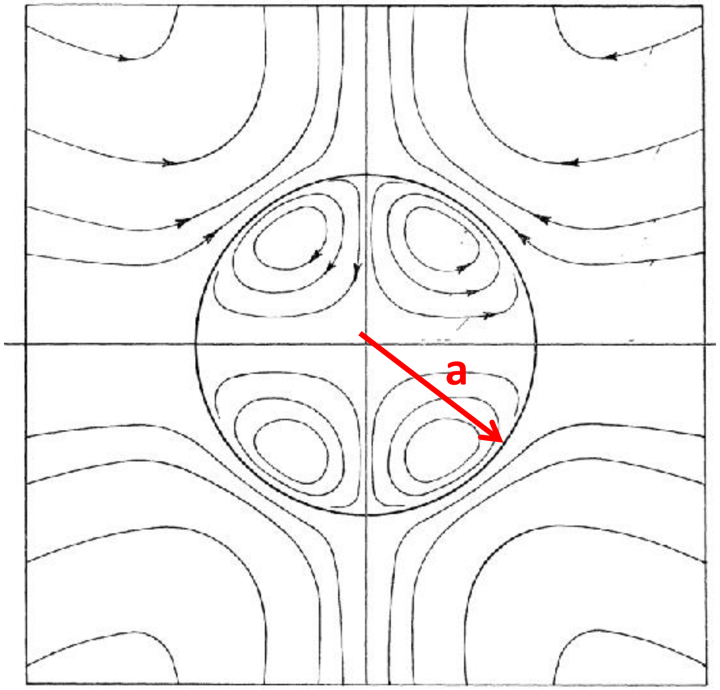
$$\mathbf{T}_{Maxwell} = \varepsilon\left(\boldsymbol{E}\boldsymbol{E} - \frac{1}{2} E^2 \mathbf{I}\right)$$

Melcher and Taylor (1969)

Taylor EHD model prediction for leaky-dielectric drops:

Hydrodynamic surface flow due to electric surface stress

$$v_\theta = -\frac{9}{40\pi(\eta+\hat{\eta})}\frac{a\hat{\varepsilon}E^2}{\left(2+\frac{\hat{\sigma}}{\sigma}\right)^2}\left(\frac{\tau}{\hat{\tau}}-1\right)\cos 2\theta$$



Drop deformation:

$$D = \frac{9}{16}\frac{R\varepsilon E_\infty^2}{\gamma}\Phi\left(\frac{\hat{\varepsilon}}{\varepsilon},\frac{\hat{\sigma}}{\sigma},\frac{\hat{\eta}}{\eta}\right)$$

The model predicts $D<0$ for silicon oil in castor oil , and $D>0$ for castor oil in silicon oil in agreement with experiments. Note that the time it takes for 1 turn a/v_θ independent of a)

Condition 1: Two leaky dielectric liquids

Condition 2: $\sigma_{drop} < \sigma_{surrounding}$

When DC E-field applied:

Free charge accumulation

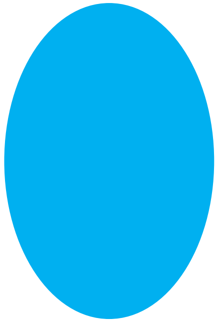
⬇

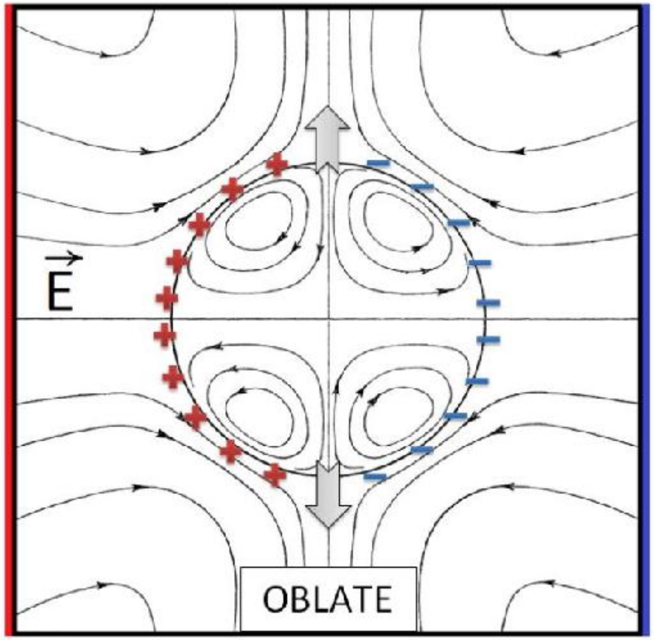
Maxwell electric stress

⬇

Liquid circulation flows

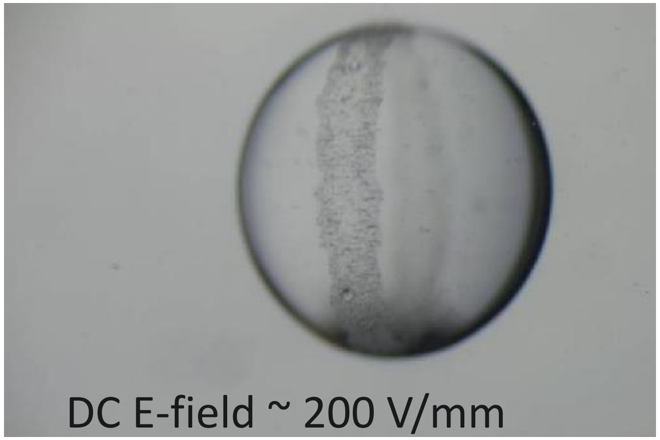
Oblate deformation





Adopted from [Taylor 1965]

Ribbon structure

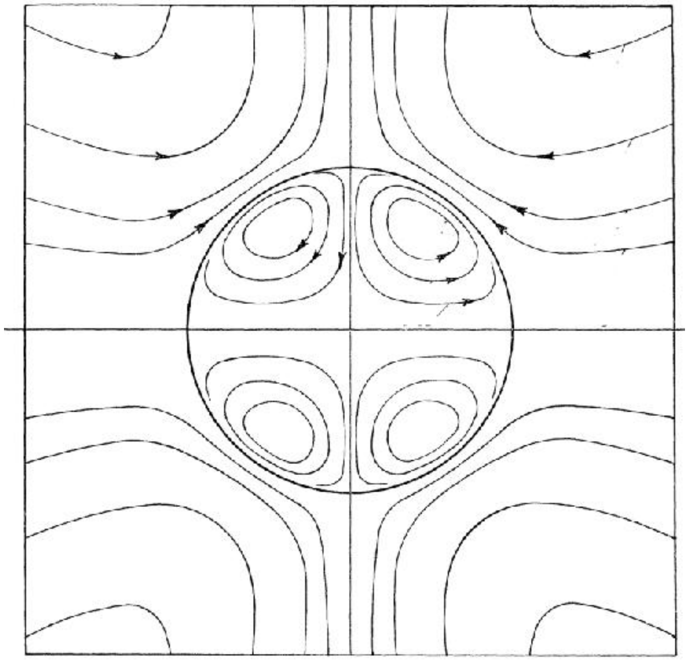


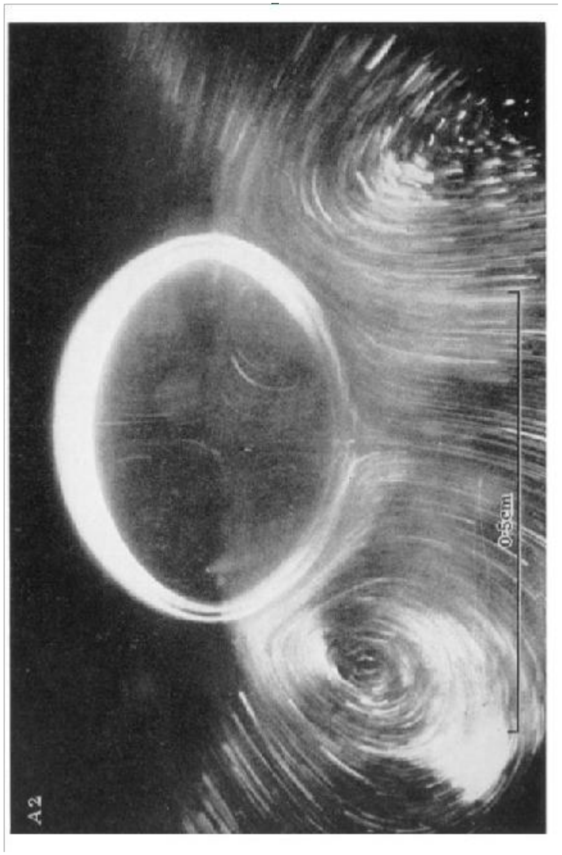
DC E-field ~ 200 V/mm

Electro-hydrodynamic Taylor flow

From Taylors original paper:

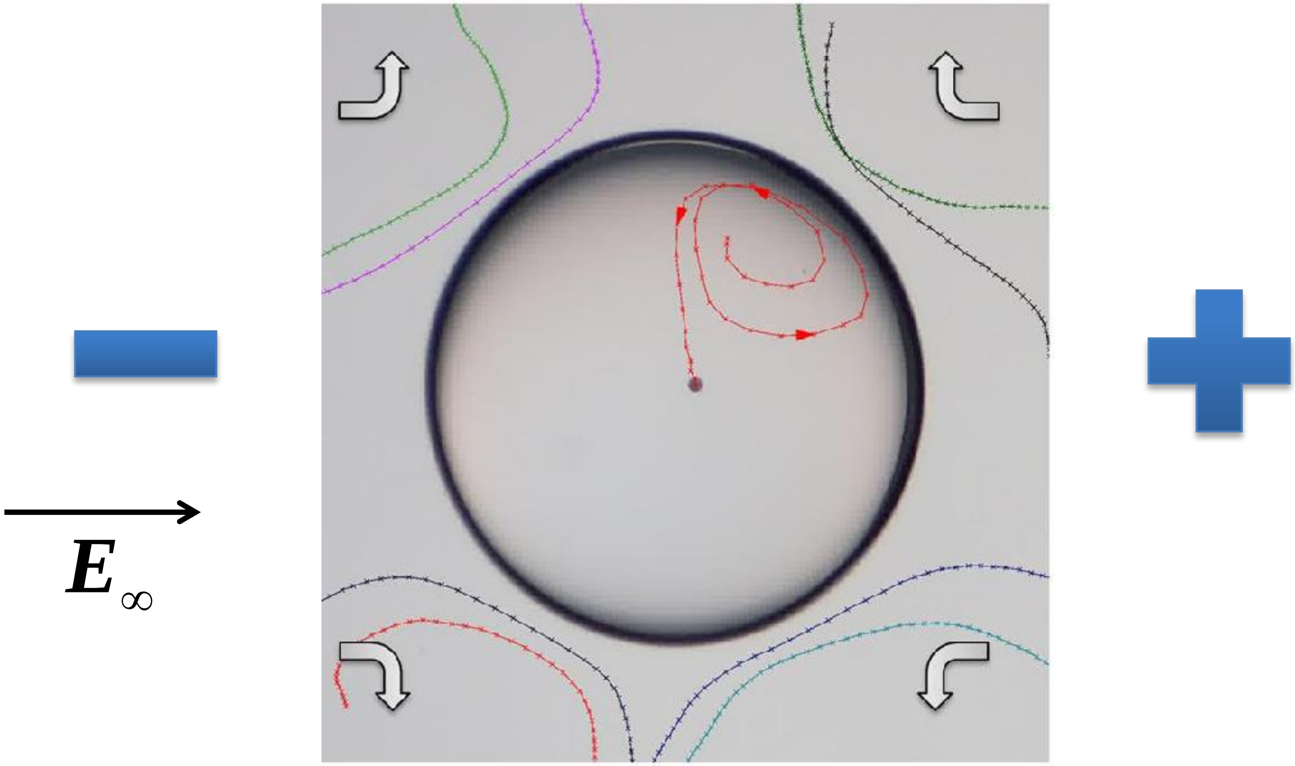
G.I. Taylor: Proc. R. Soc. Lond. A 291,159-166 (1966)





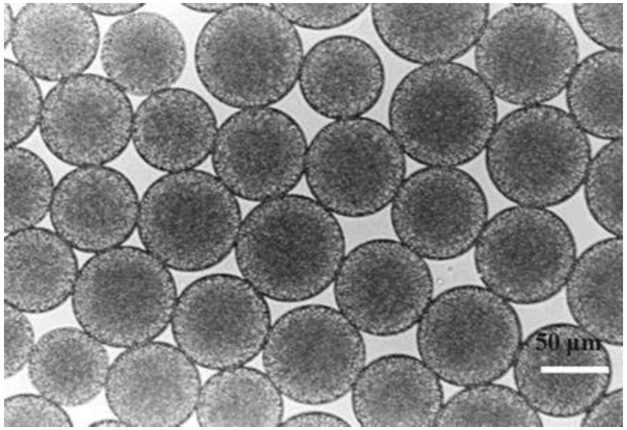
Conducting fluids

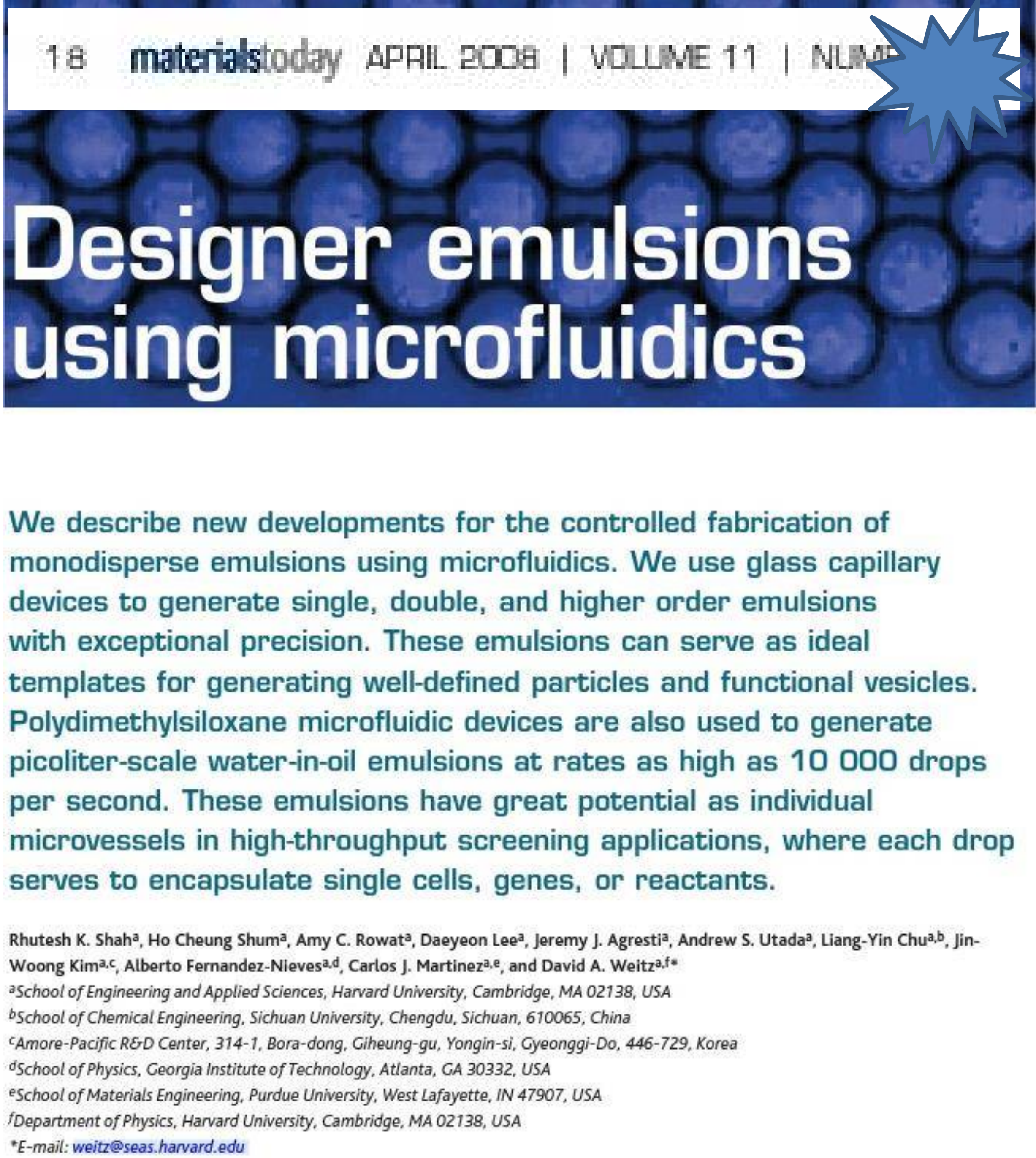
Tracing PE beads in a drop subjected to an electric field:



Electro-hydrodynamic flow: Experiments at NTNU Trondheim

Monodisperse emulsions




18 materialstoday APRIL 2008 | VOLUME 11 | NUM

Designer emulsions using microfluidics

We describe new developments for the controlled fabrication of monodisperse emulsions using microfluidics. We use glass capillary devices to generate single, double, and higher order emulsions with exceptional precision. These emulsions can serve as ideal templates for generating well-defined particles and functional vesicles. Polydimethylsiloxane microfluidic devices are also used to generate picoliter-scale water-in-oil emulsions at rates as high as 10 000 drops per second. These emulsions have great potential as individual microvessels in high-throughput screening applications, where each drop serves to encapsulate single cells, genes, or reactants.

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Monodisperse emulsions

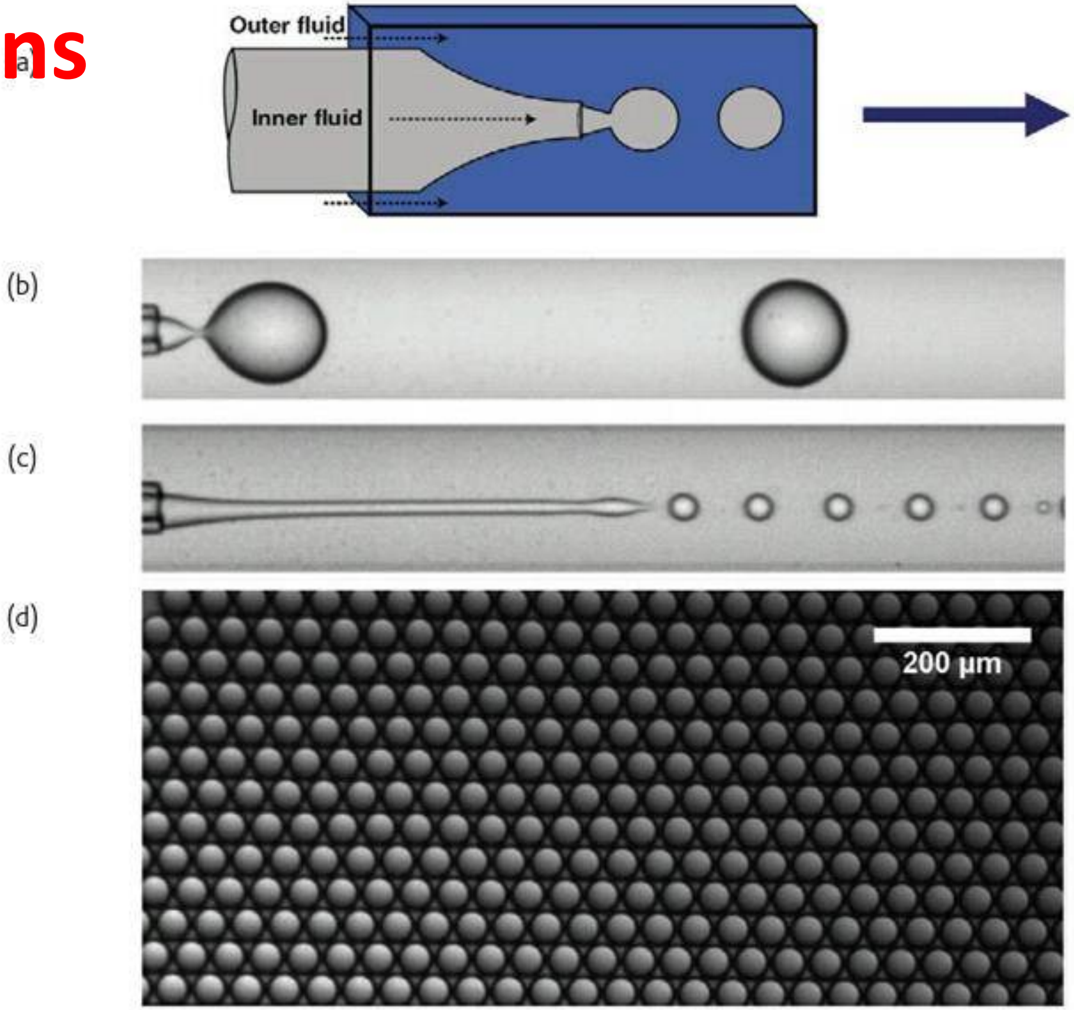
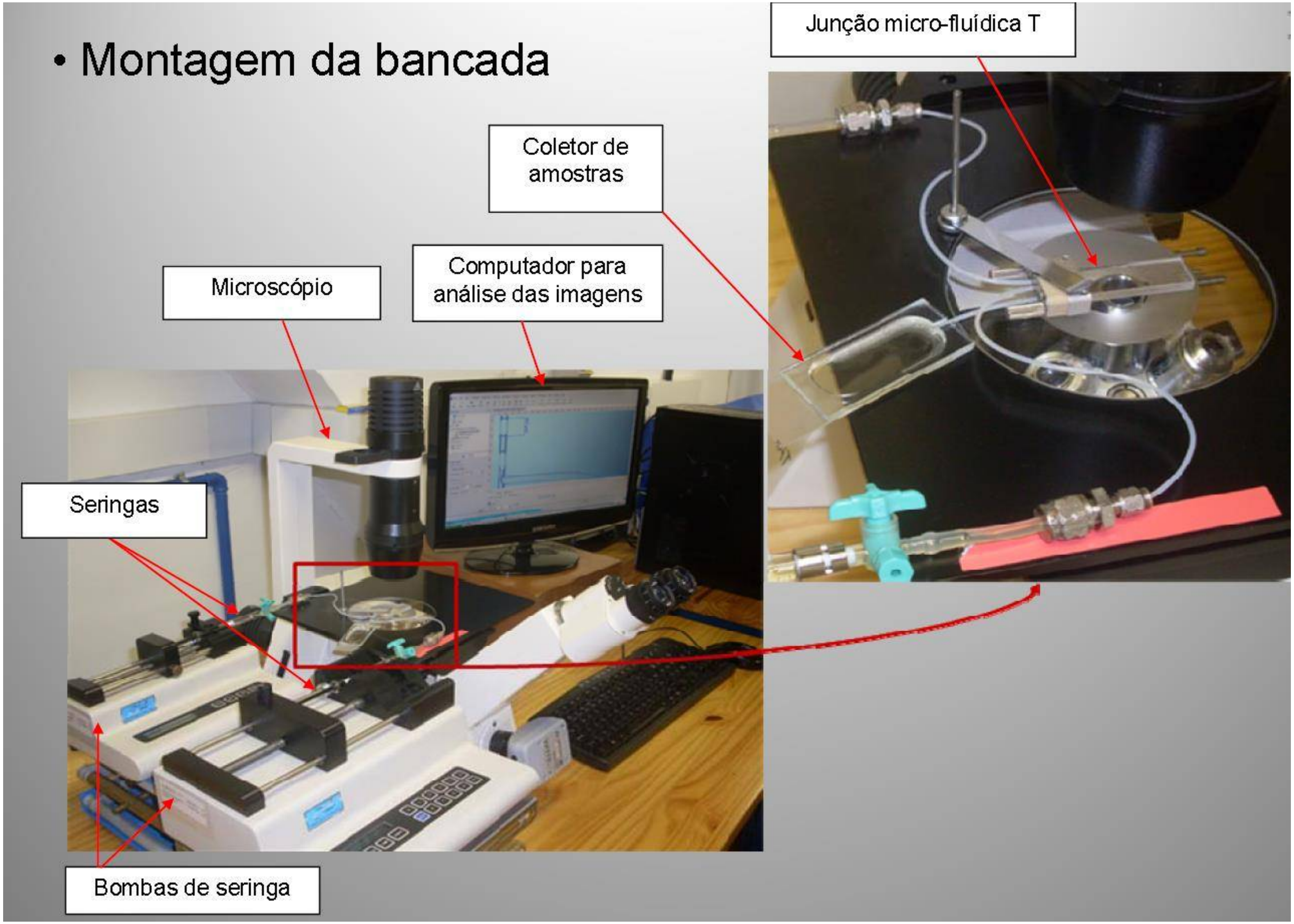


Fig. 2 Single emulsions in a co-flow microfluidic device. (a) Schematic of a co-flow microcapillary device for making droplets. Arrows indicate the flow direction of fluids and drops. (b) Image of drop formation at low flow rates (dripping regime). (c) Image of a narrowing jet generated by increasing the flow rate of the continuous fluid above a threshold value while keeping the flow rate of the dispersed phase constant. (d) Monodisperse droplets formed using a microcapillary device. [Part (a) reproduced with permission from[26]*. © 2007 Materials Research Society; parts (b) and (c) reprinted with permission from*[27]*. © 2007 American Physical Society.]*

Table-top experiment:



- Montagem da bancada

Junção micro-fluídica T

Coletor de amostras

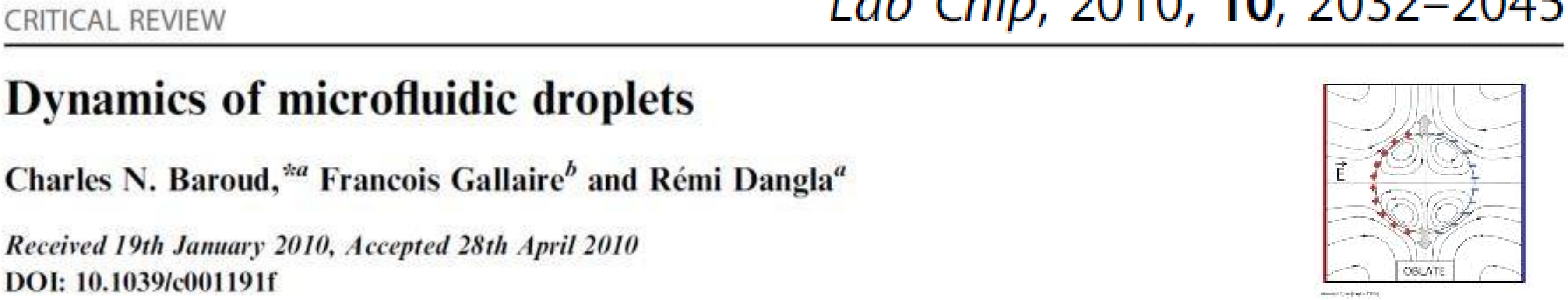
Computador para análise das imagens

Microscópio

Seringas

Bombas de seringa

Lab Chip, 2010, **10**, 2032–2045

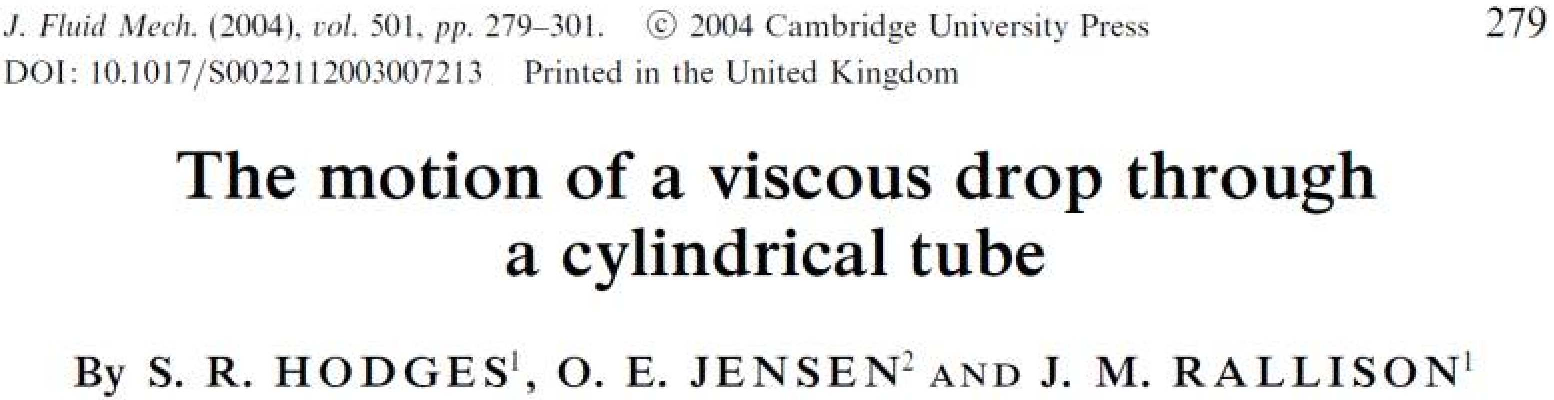


CRITICAL REVIEW

Dynamics of microfluidic droplets

Charles N. Baroud,[*a] **Francois Gallaire**[b] **and Rémi Dangla**[a]

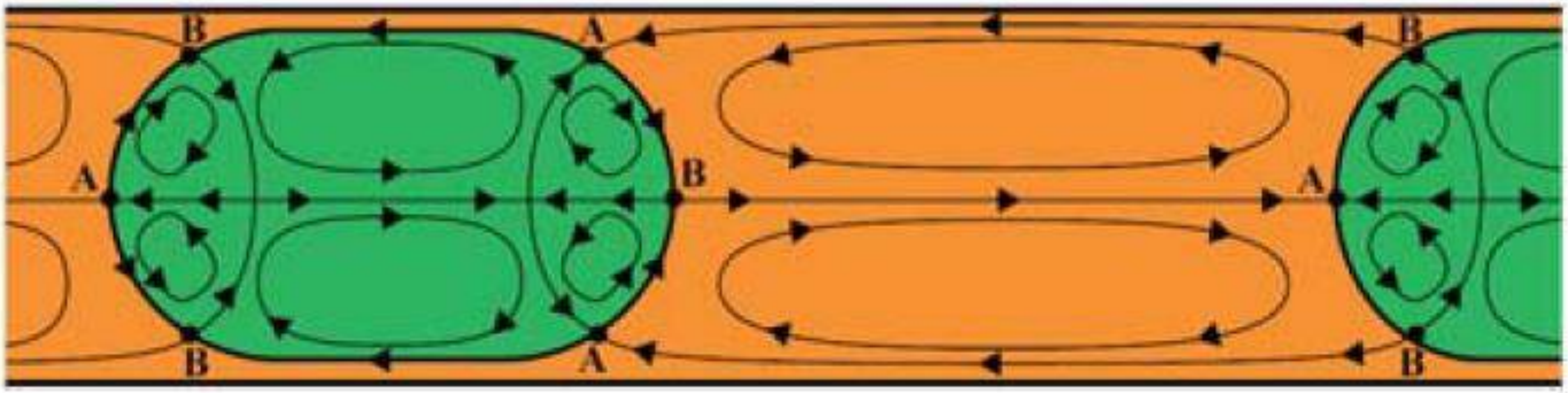
Received 19th January 2010, Accepted 28th April 2010
DOI: 10.1039/c001191f



J. Fluid Mech. (2004), *vol.* 501, *pp.* 279–301. © 2004 Cambridge University Press
DOI: 10.1017/S0022112003007213 Printed in the United Kingdom

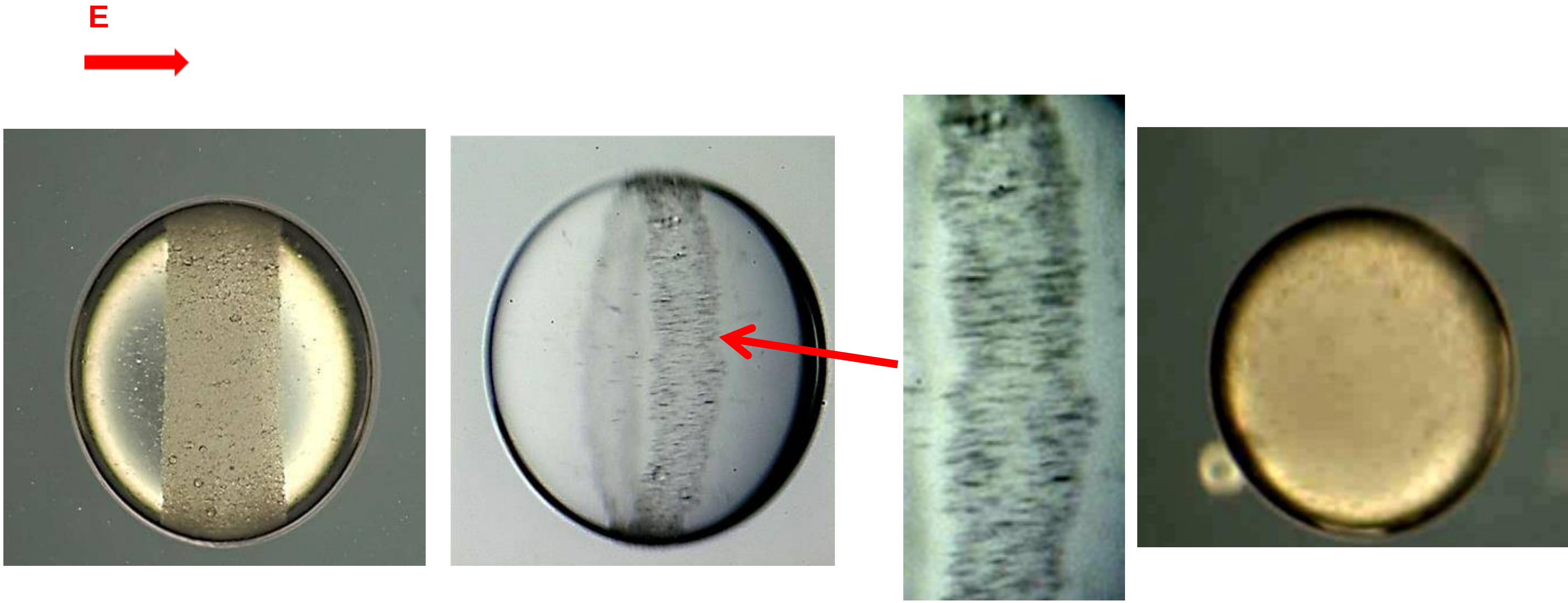
The motion of a viscous drop through a cylindrical tube

By S. R. HODGES[1], O. E. JENSEN[2] AND J. M. RALLISON[1]

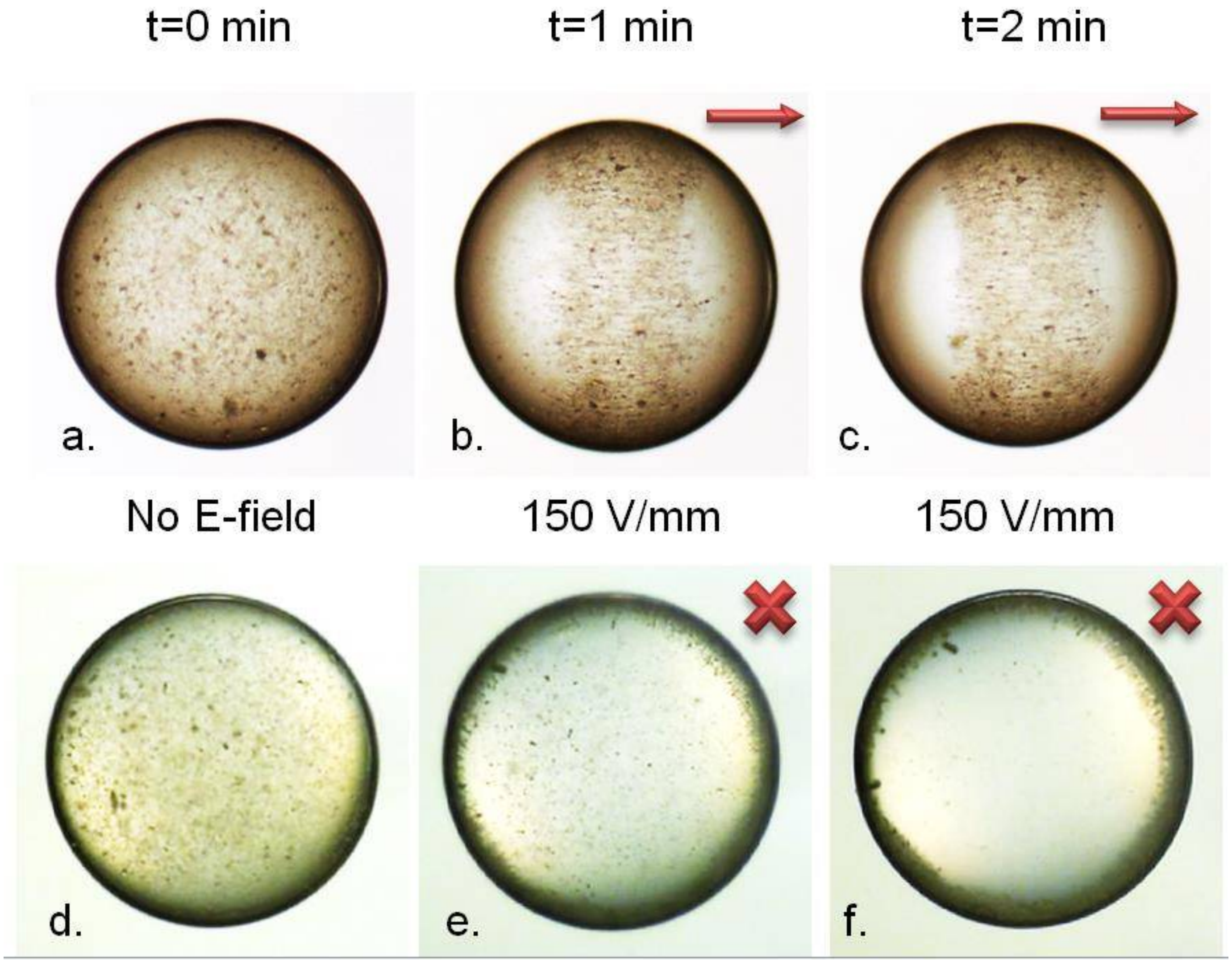


for low viscosity ratio

Clay-oil drop in electric fields



- Clay particles goes to the surface of the drop.
- Particles form a ribbon.
- Electro-rheological chains in the ribbon.
- Flow field inside drop

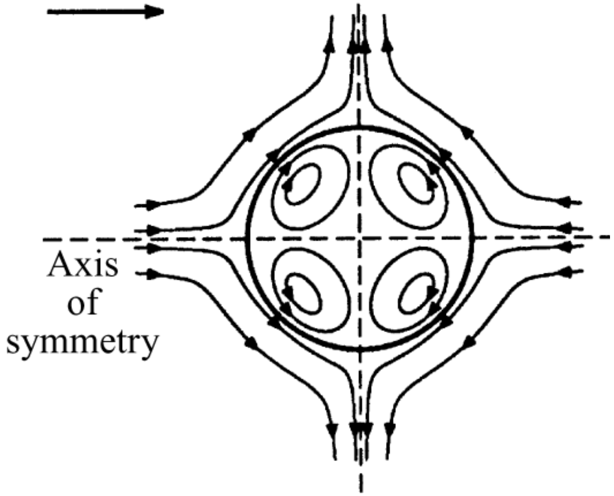


Ribbon-like structure: Experiments at NTNU Trondheim

Maxwell times determines direction of flow

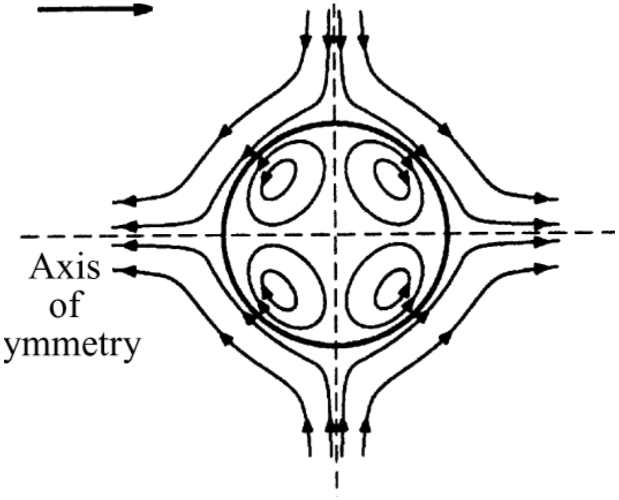
$$v_\theta = -\frac{9}{40\pi(\eta+\hat{\eta})} \frac{a\hat{\varepsilon}E^2}{\left(2+\frac{\hat{\sigma}}{\sigma}\right)^2} \left(\frac{\tau}{\hat{\tau}} - 1\right) \cos 2\theta$$

$\hat{\tau} > \tau$



Flow towards equator

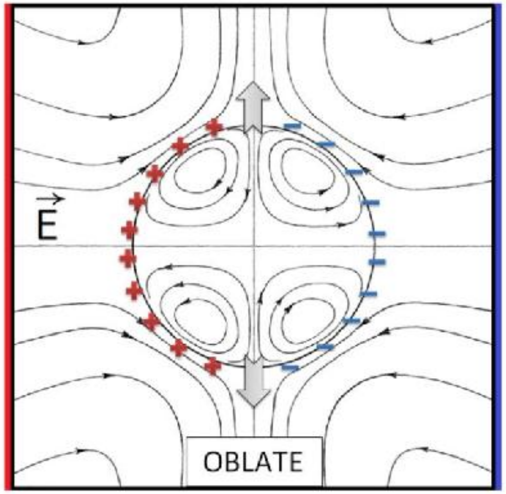
$\hat{\tau} < \tau$



Flow towards poles

Our Condition 1: Two leaky dielectric liquids

Our Condition 2: $\sigma_{drop} < \sigma_{surrounding}$

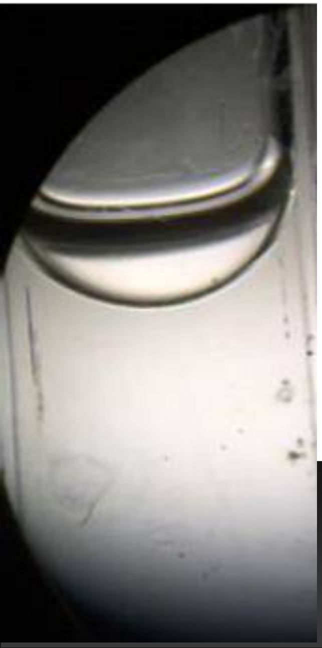


If insted $\sigma_{drop} > \sigma_{surrounding}$

then the flow is reversed and the particles are transported to the **electrical poles** rather than to the electrical equator

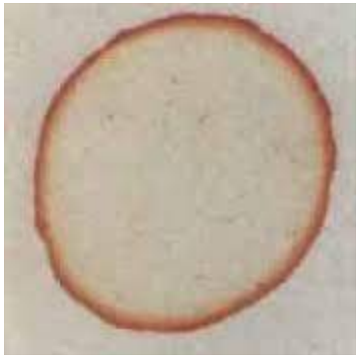
Colloidal caps

Drop fluid



Electro-hydrodynamic flow

Coffe ring effect:
Convective deposition by hydrodynamic flow
(No direct electrical forces on particles)

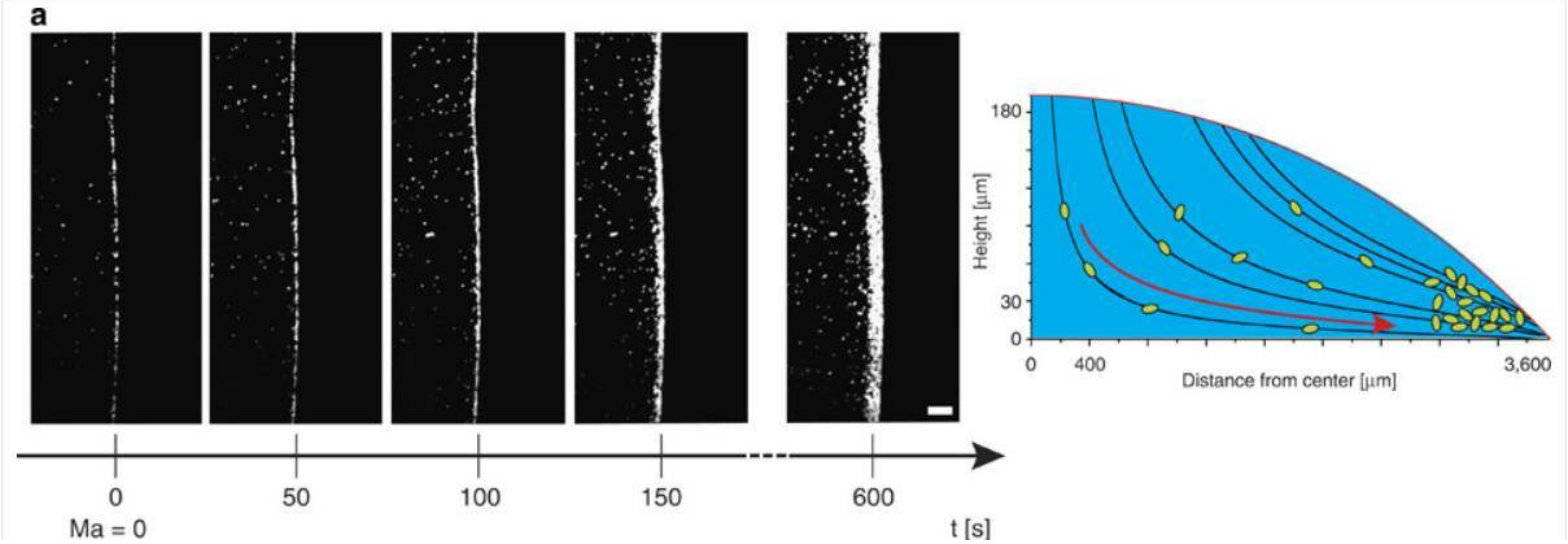


From

Auto-production of biosurfactants reverses the coffee ring effect in a bacterial system

Wouter Sempels, Raf De Dier, Hideaki Mizuno, Johan Hofkens & Jan Vermant

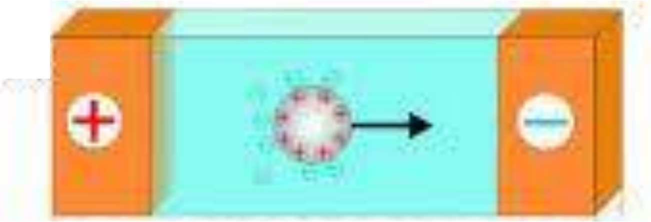
Nature Communications **4**, Article number: 1757 | doi:10.1038/ncomms2746



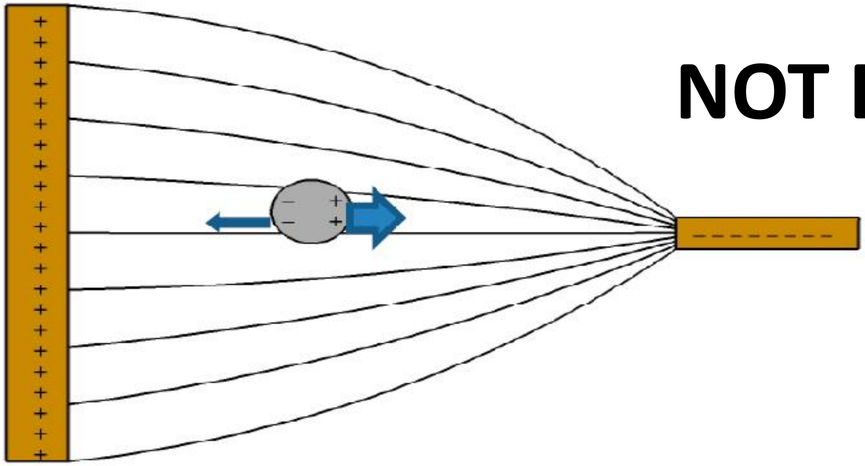
R. D. Deegan, O. Bakajin, T. F. Dupont, G. Huber, S. R. Nagel, T. A. Witten (1997). "Capillary flow as the cause of ring stains from dried liquid drops". *Nature* **389** (6653): 827–829

There are weak direct electrical forces on our particles

Convective deposition dominates here:

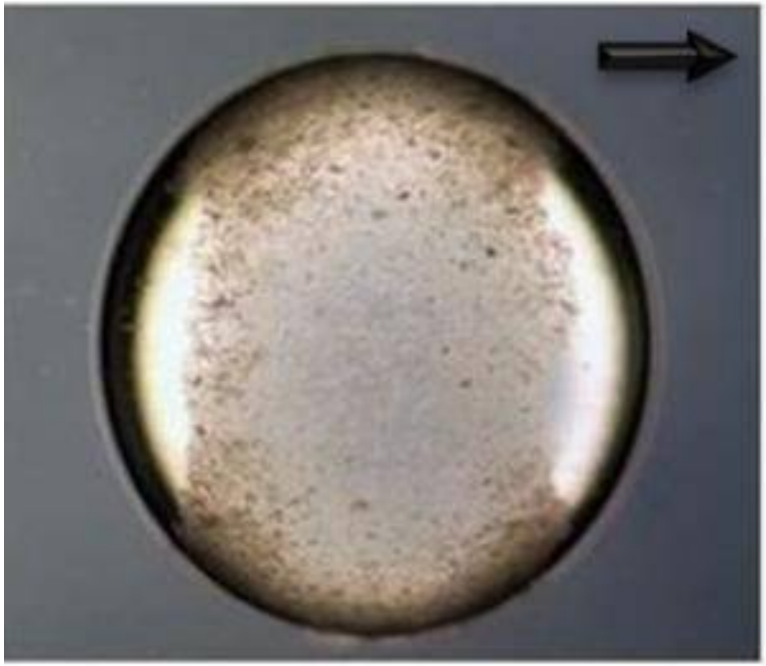


NOT Electrophoresis



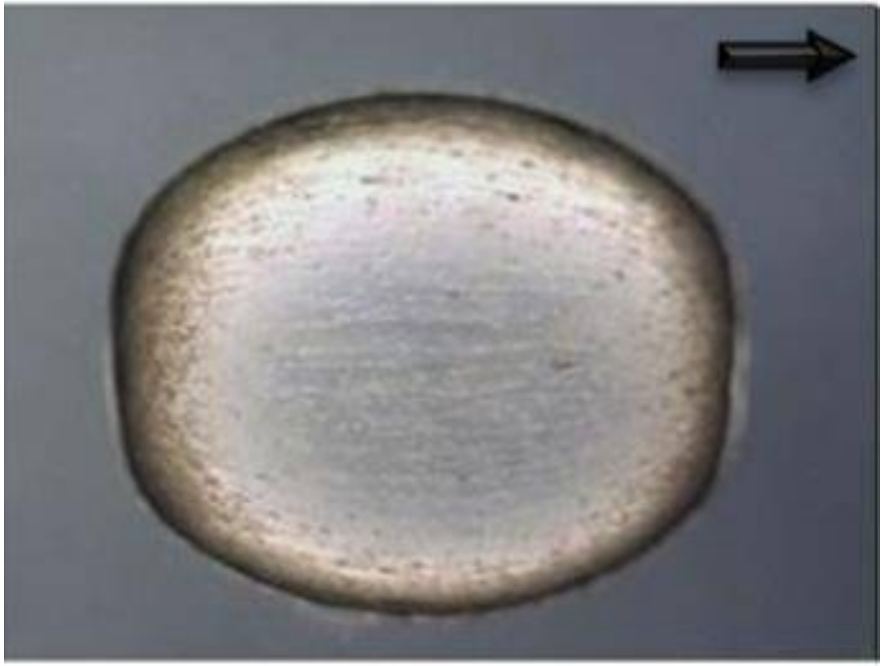
NOT Dielectrophoresis

Oblate-to-Prolate transition



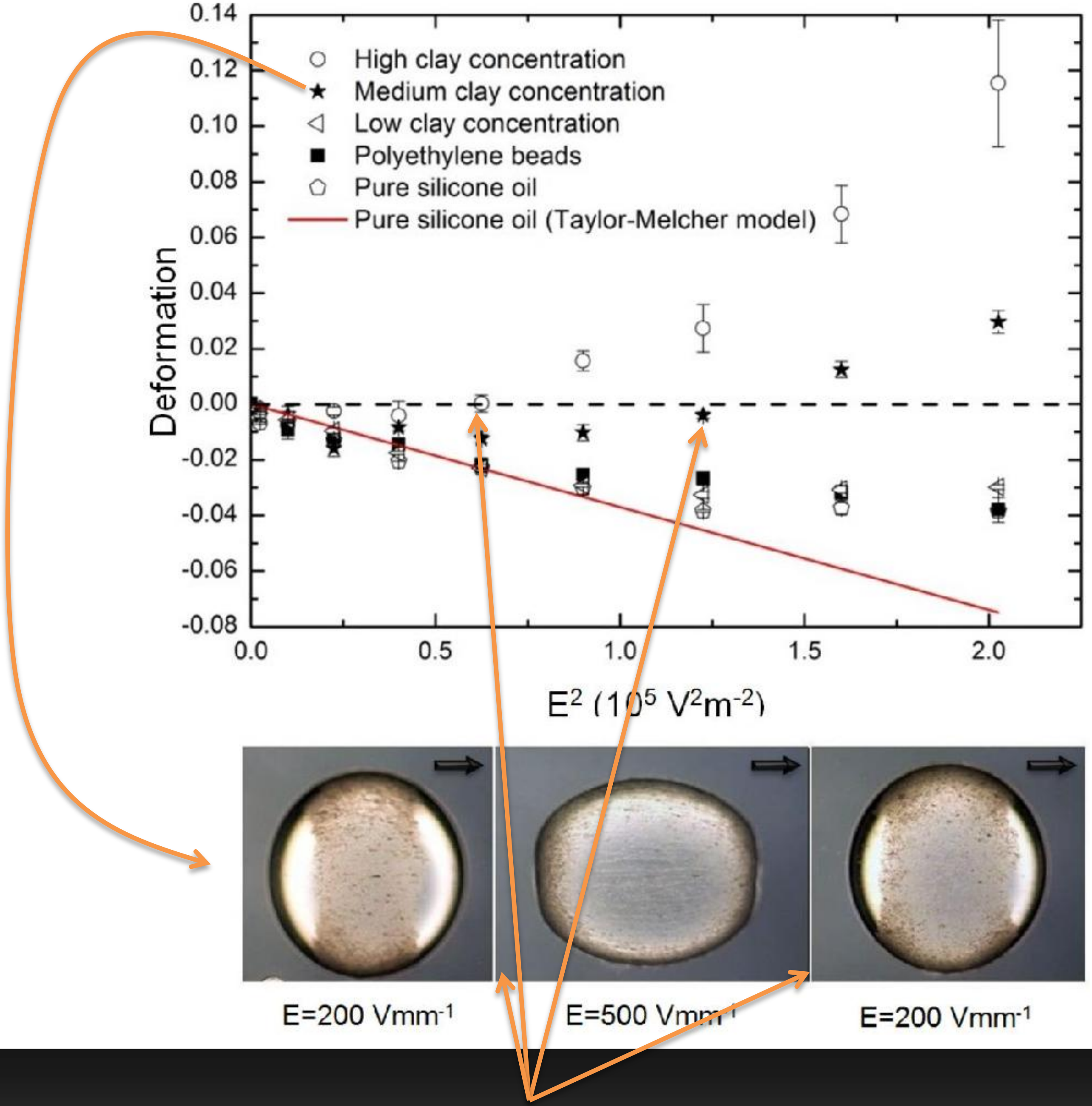
$E=200\ \mathrm{Vmm}^{-1}$

Electro-hydrodynamic flow



$E=500\ \mathrm{Vmm}^{-1}$

Dipole-dipole interactions



Oblate-to-Prolate transition

Pickering («physical») emulsions