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

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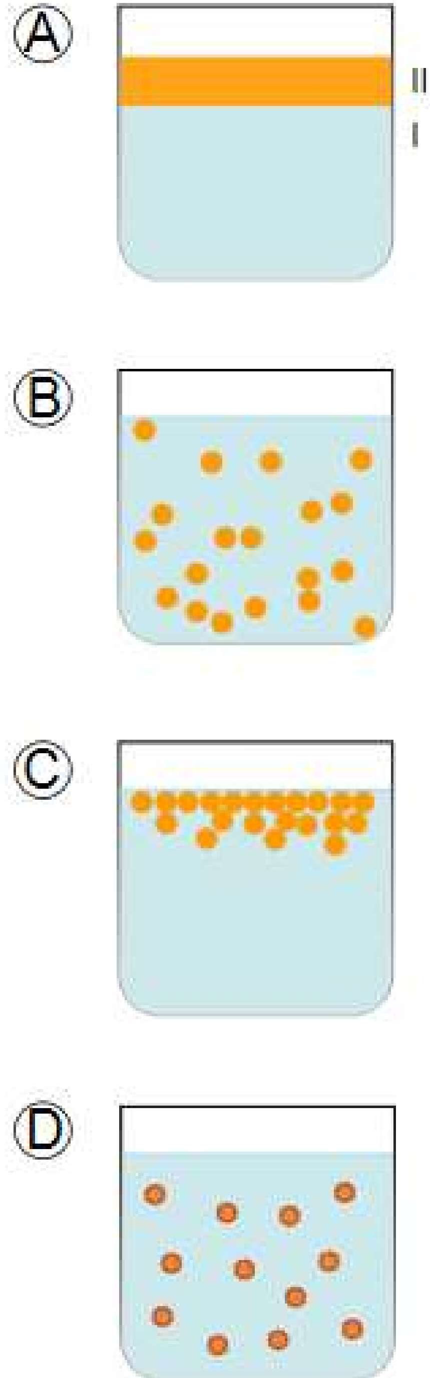
Emulsions (= Systems of MANY drops) are important in many every day and industrial contexts such as:

- 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.

NTNU

«Classical» («chemical») emulsions



Legend

- Phase I
- Phase II
- Surfactant

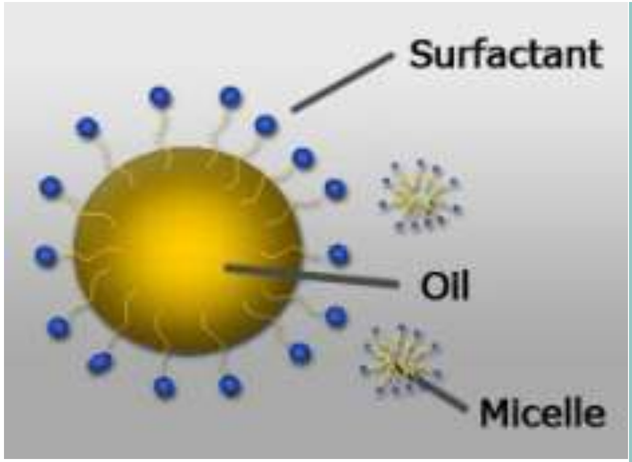
A. Two immiscible liquids, not emulsified

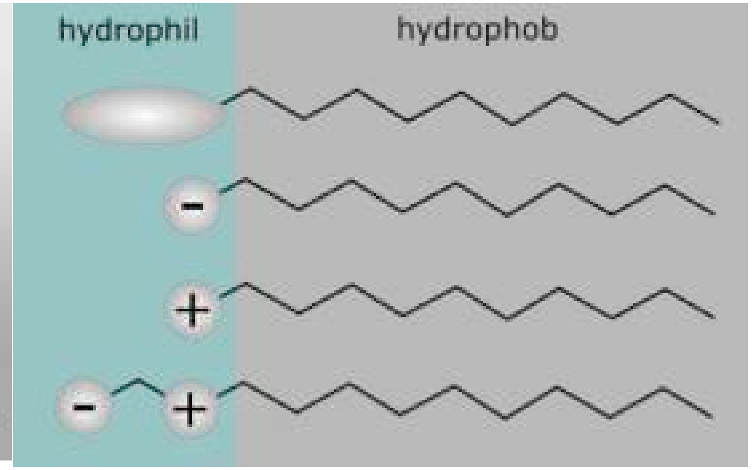
B. Emulsion of Phase II dispersed in Phase I

C. The unstable emulsion progressively separates

D. Surfactant positions itself on interface between Phases I and II, stabilizing emulsion

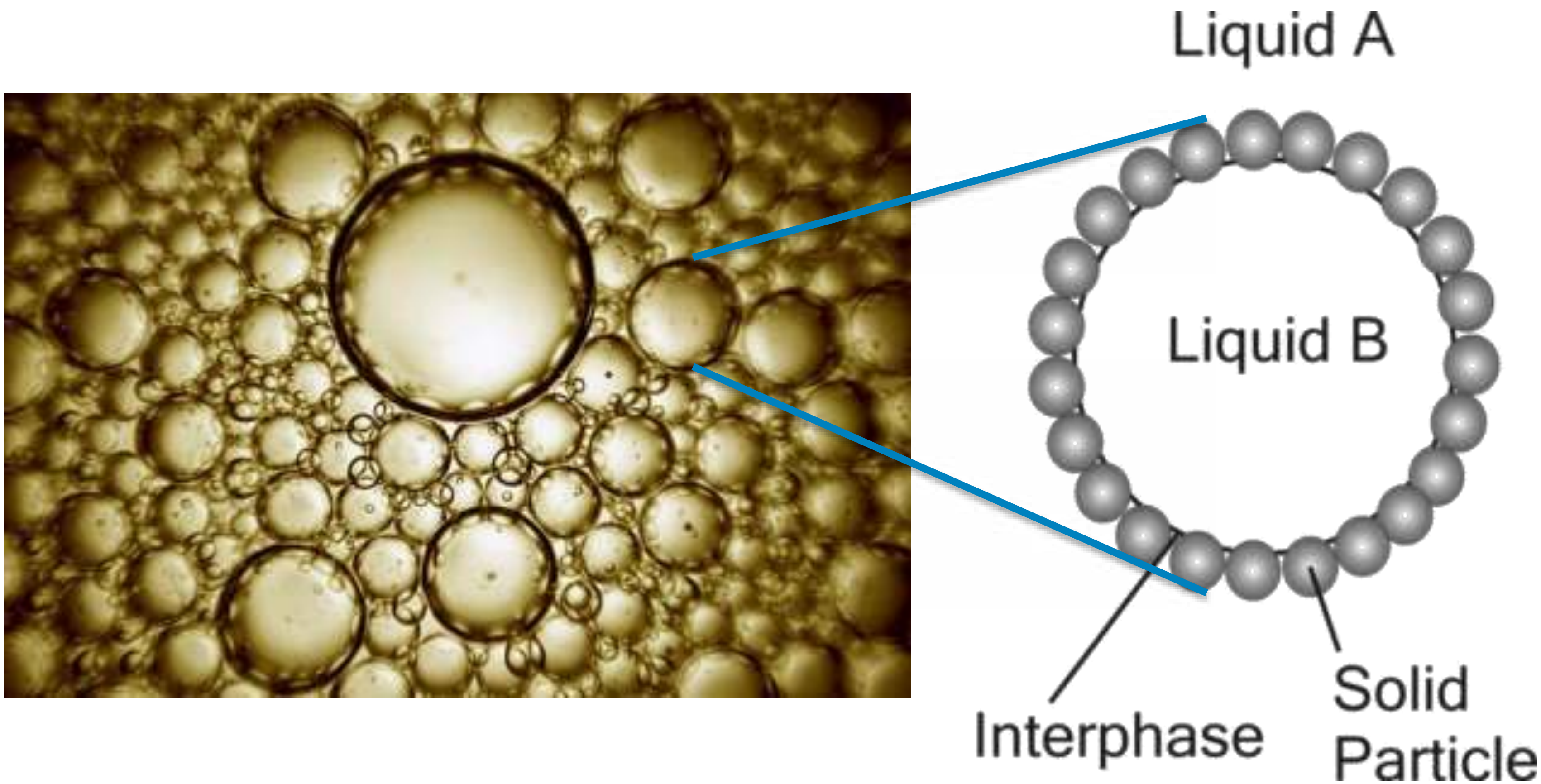
$E_{bind} > \sim k_B T$



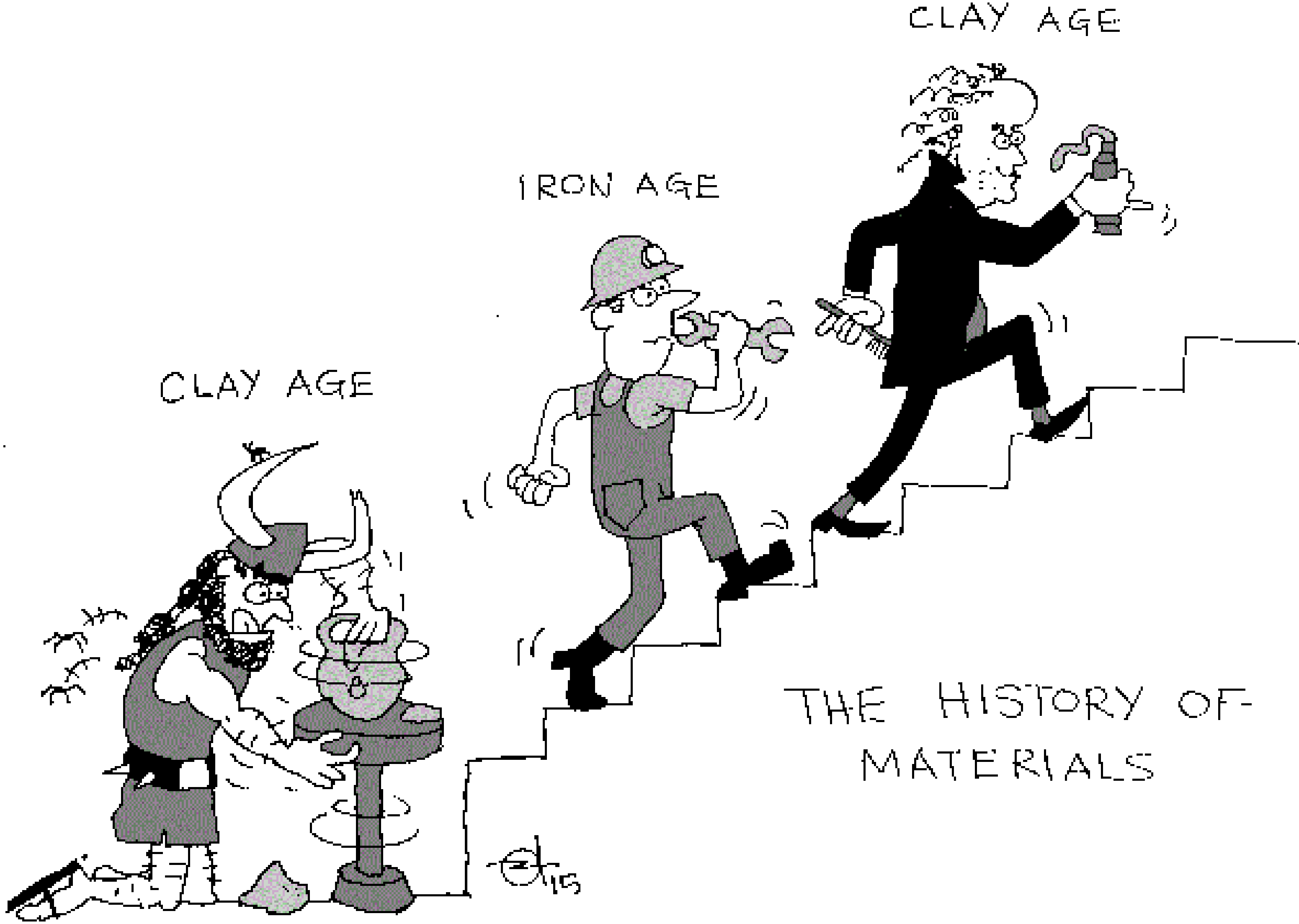


«Classical» («chemical») emulsions

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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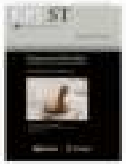
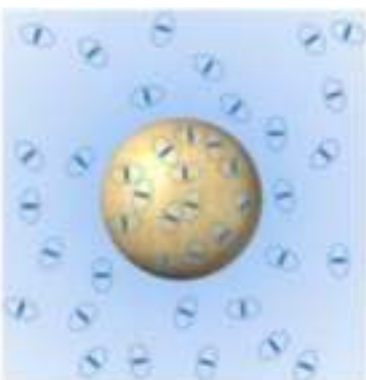


The European Physical Journal Special Topics
July 2016, Volume 225, Issue 4, pp 757–765

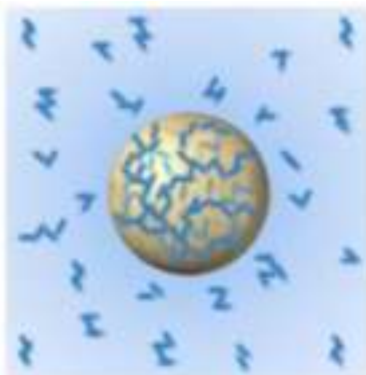
Controlled microfluidic emulsification of oil in a clay nanofluid: Role of salt for Pickering stabilization

Authors | Authors and affiliations

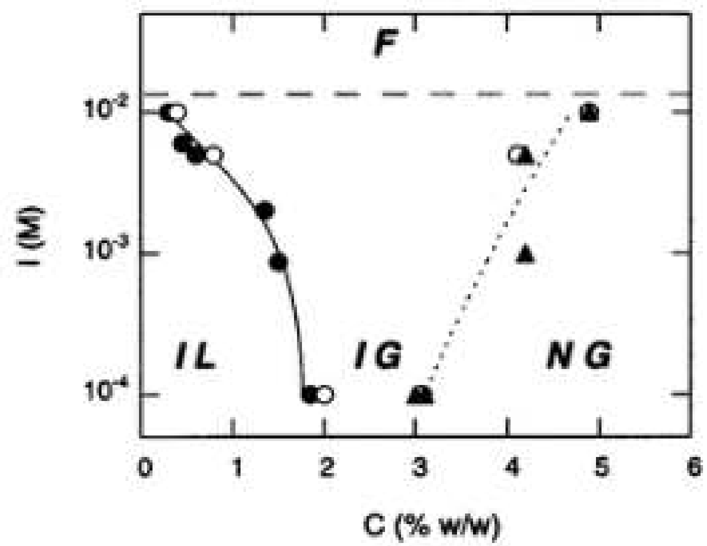
A. Gholamipour-Shirazi, M.S. Carvalho, J.O. Fossum



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



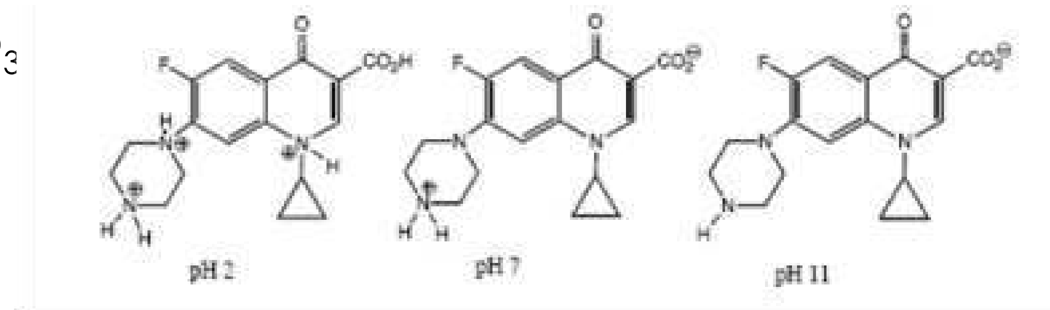
With salt:
~ 4 μm Pickering film.
Increased surface tension.



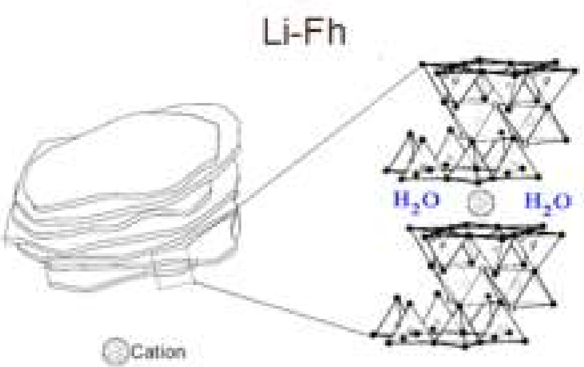
Cipro (ciprofloxacin) is an antibiotic in a group of drugs called fluoroquinolones (flor-o-KWIN-o-lones). It is used to fight bacteria in the body. Cipro is used to treat different types of bacterial infections. It may also be used to prevent or slow anthrax after exposure.

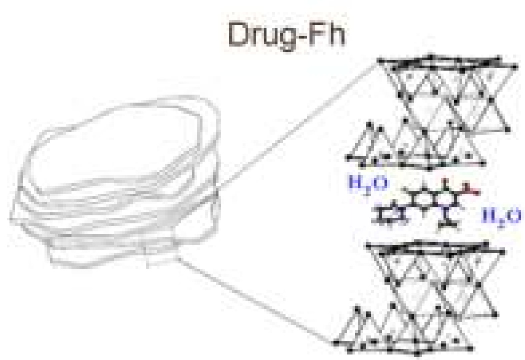
$C_{17}H_{18}FN_3O_3$

Zwitterionic



Positive **Dipole** **Negative**





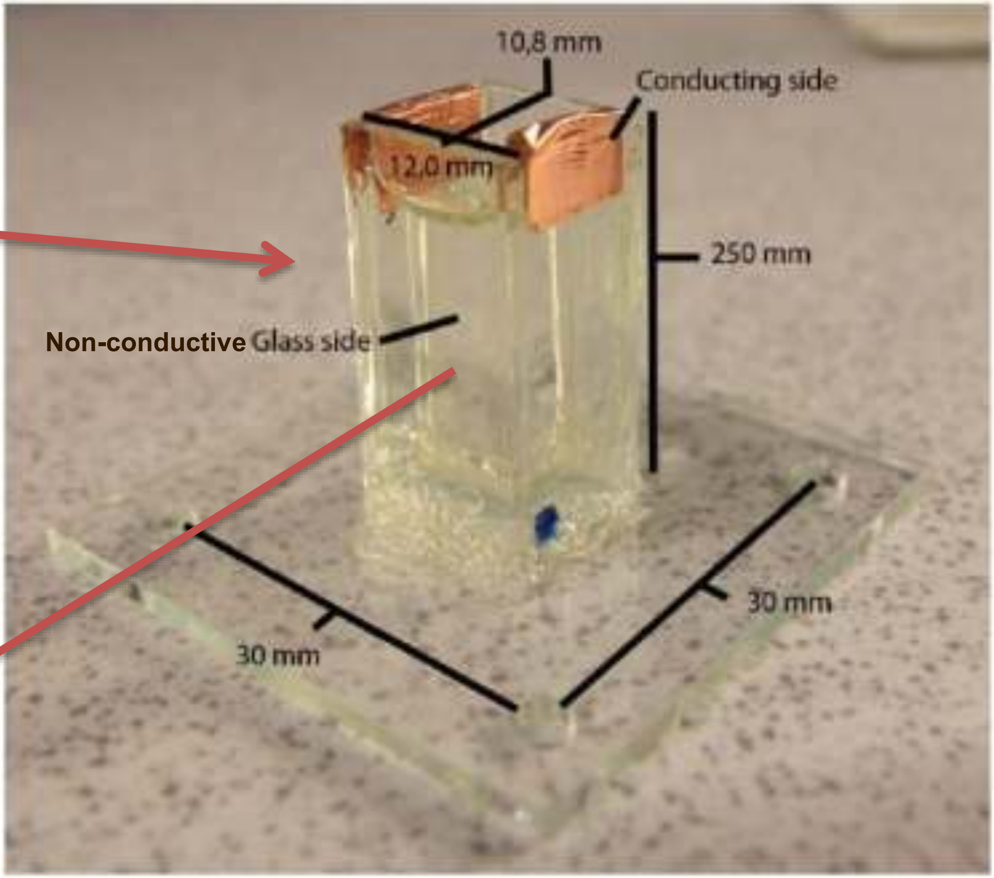
Intercalates by far best for acid pH

Different intercalation mechanism at pH 7?

Rapid release at basic pH

Techniques: XRD, UV-VIS Spectroscopy

Sample cell

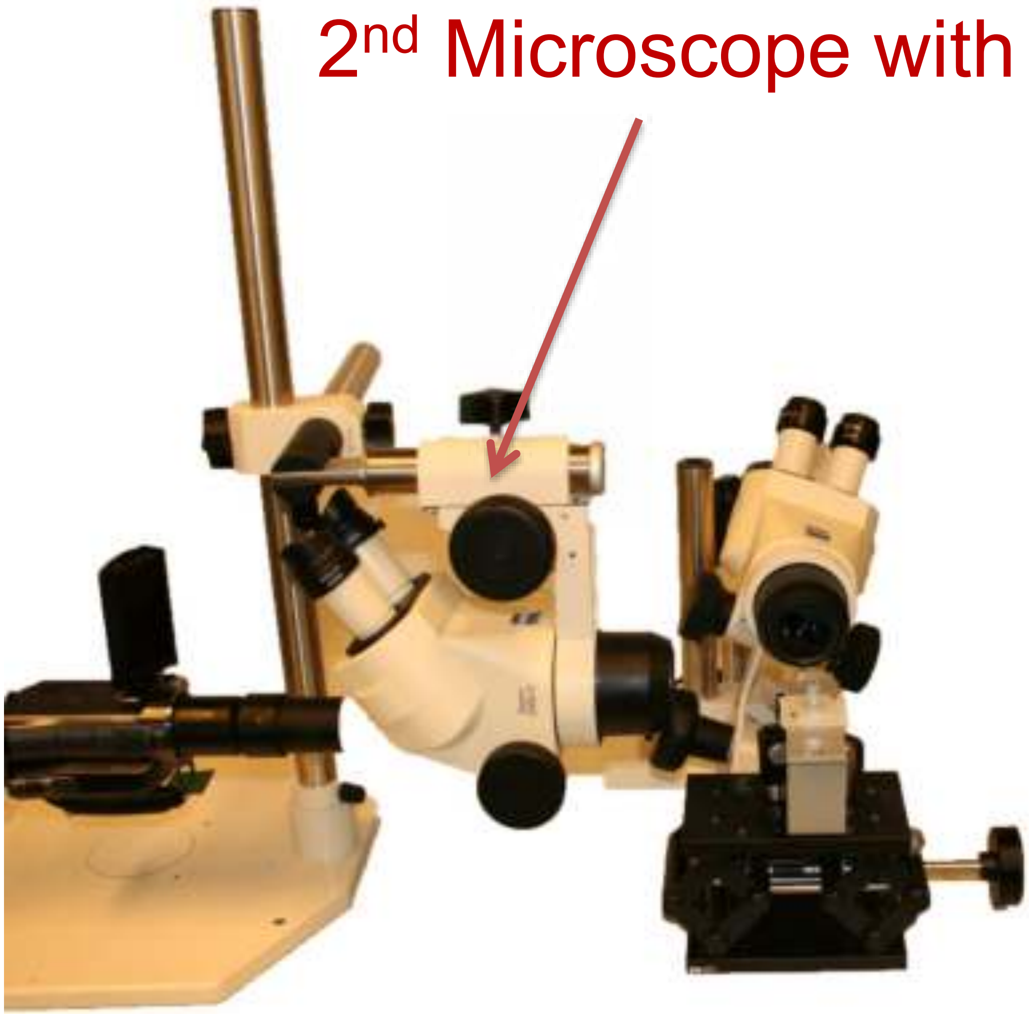


Translation stages

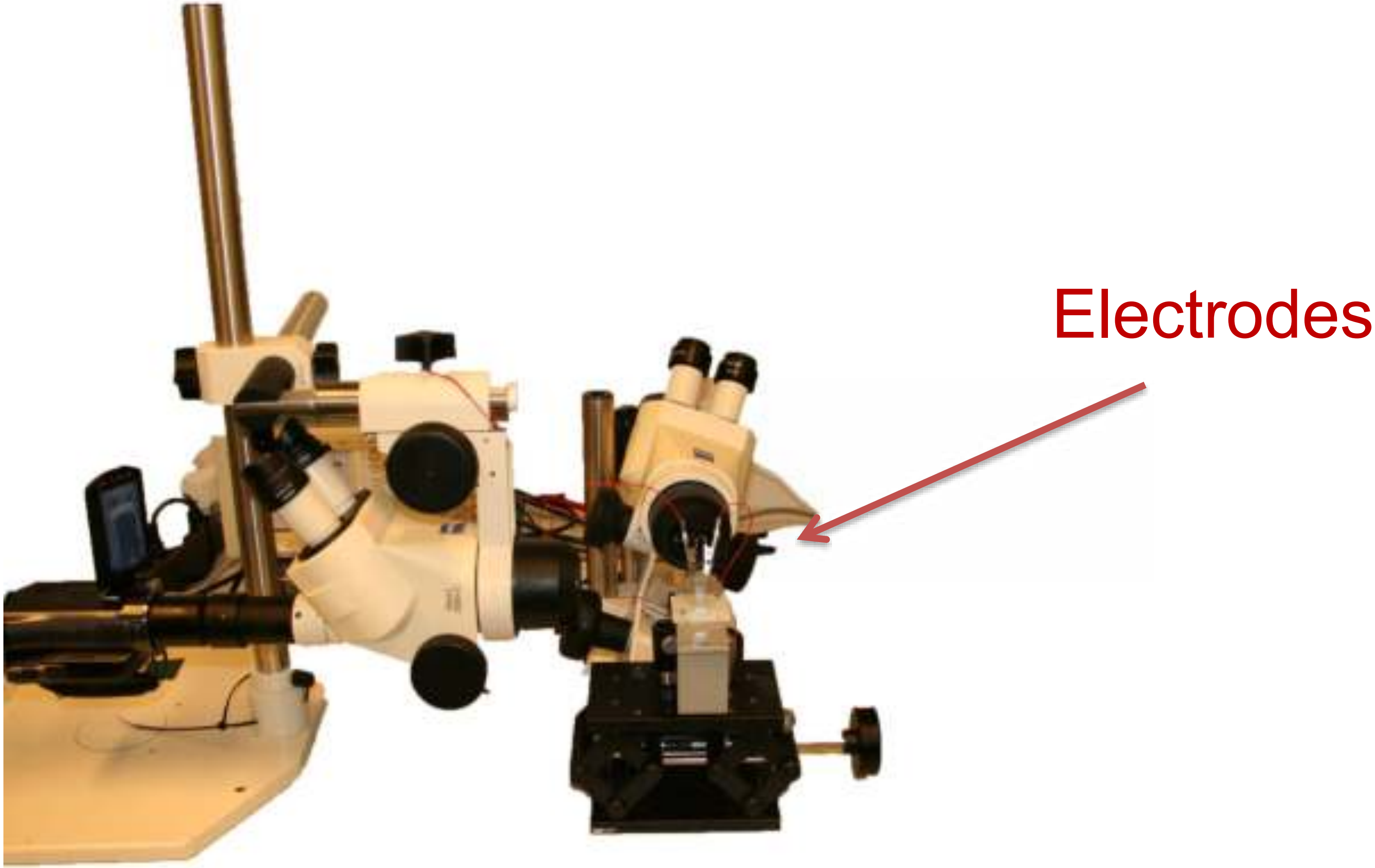
Experimental setup at NTNU Trondheim

1st Microscope with camera

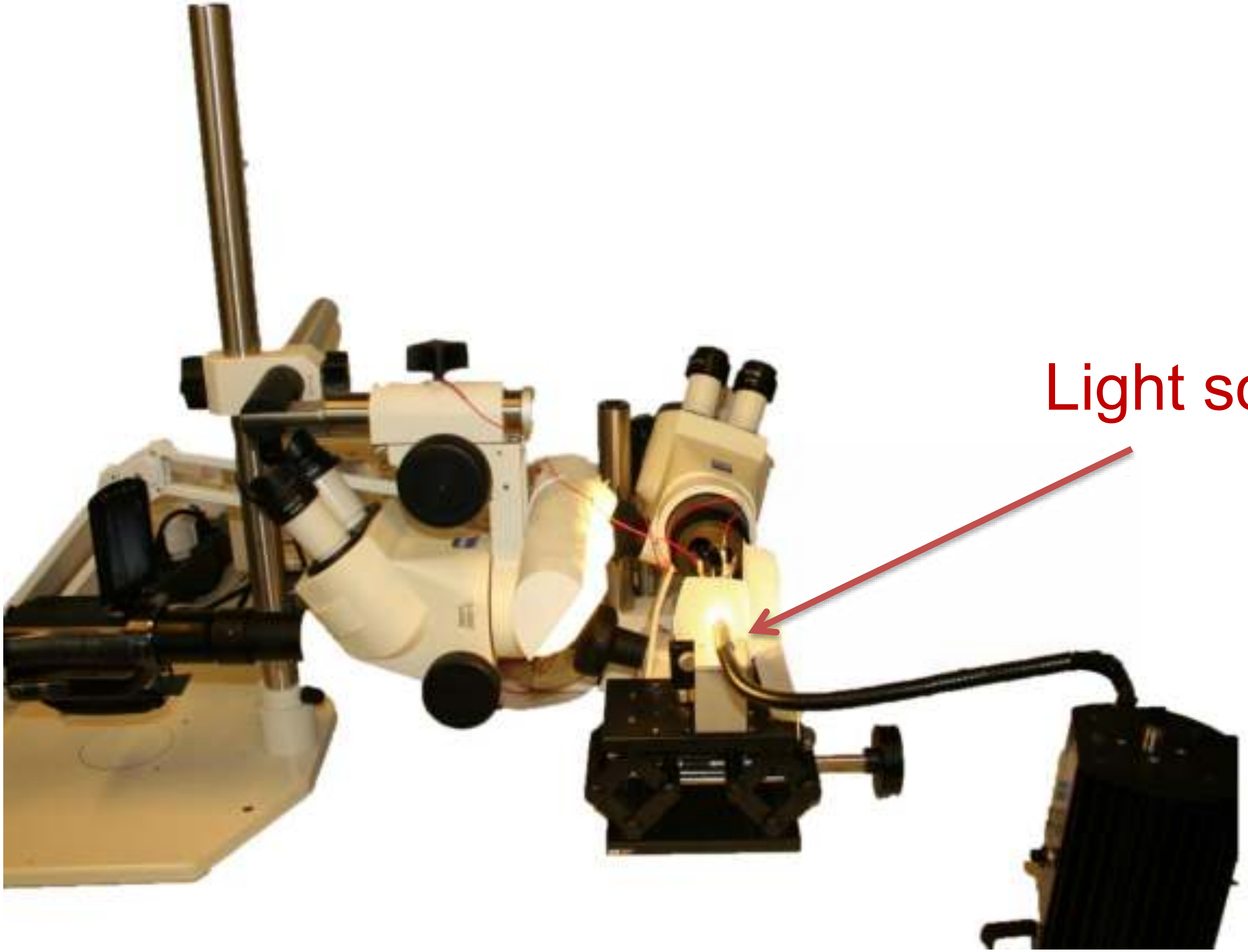
2nd Microscope with camera



Experimental setup at NTNU Trondheim

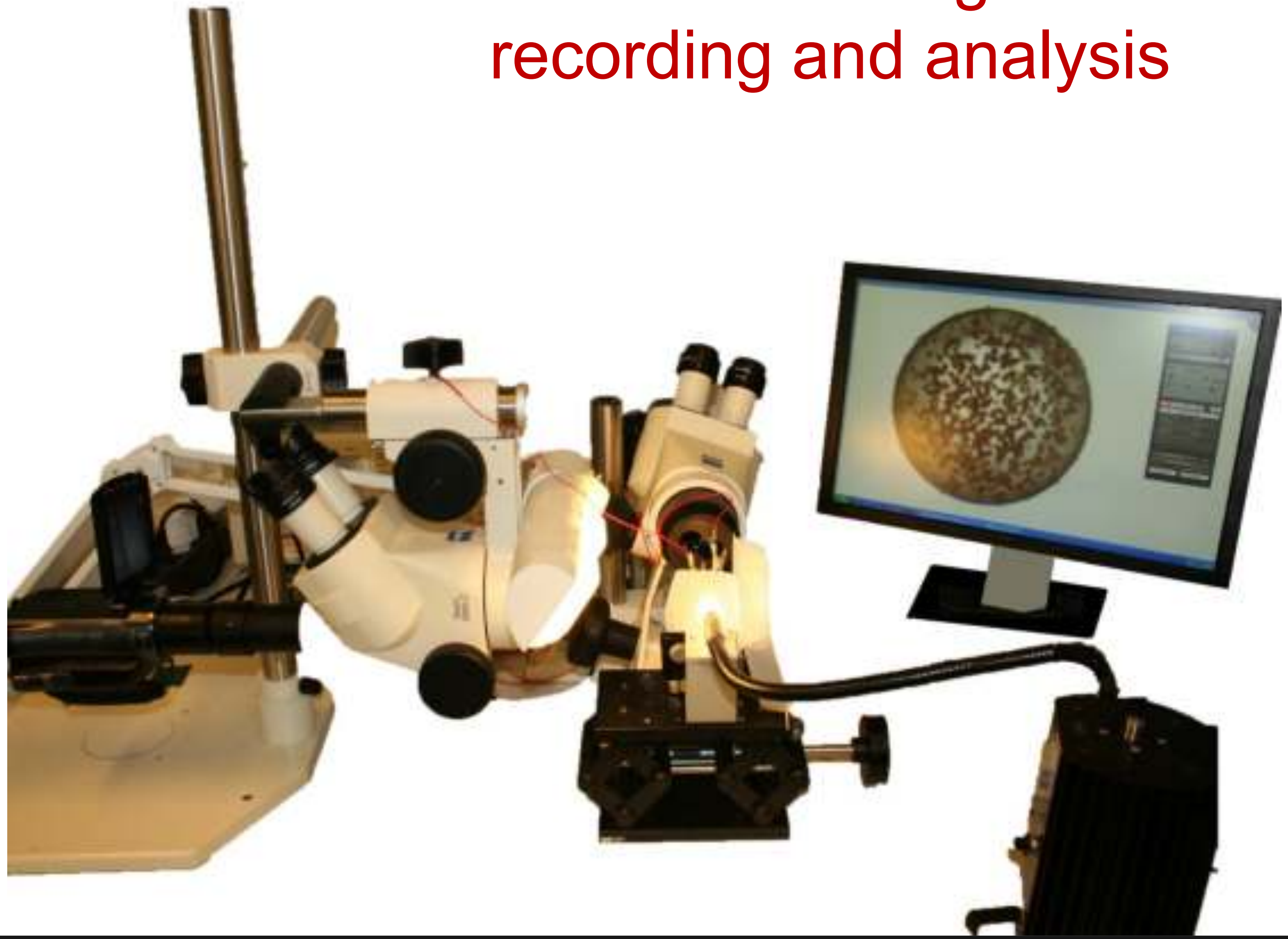


Experimental setup at NTNU Trondheim



Experimental setup at NTNU Trondheim

PC for image
recording and analysis



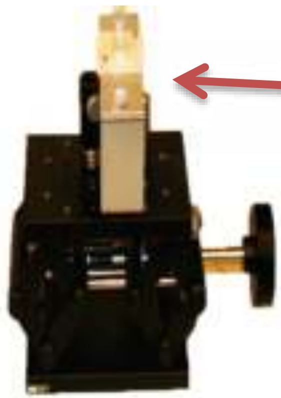
Experimental setup at NTNU Trondheim

What did we see under the microscope?

Sample cell

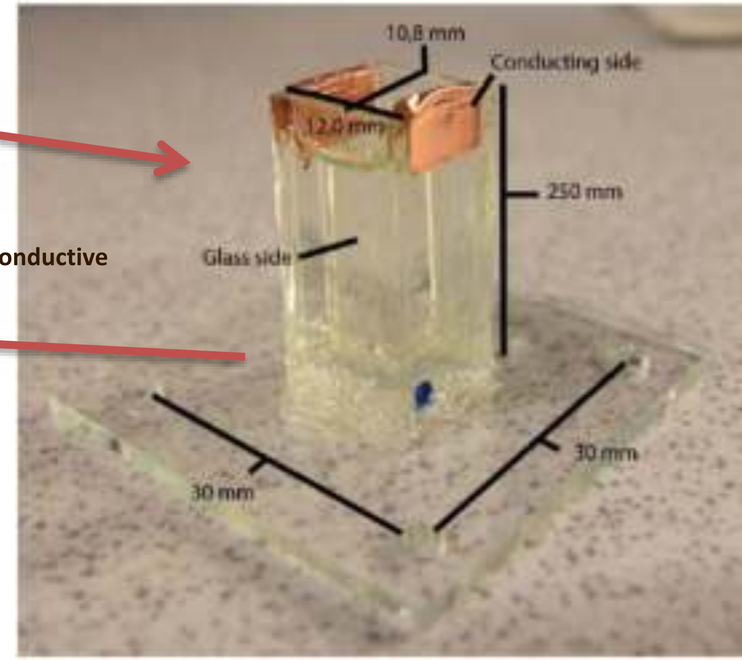
2x ITO transparent electrodes

2x glass walls



Translation stages

Non-conductive

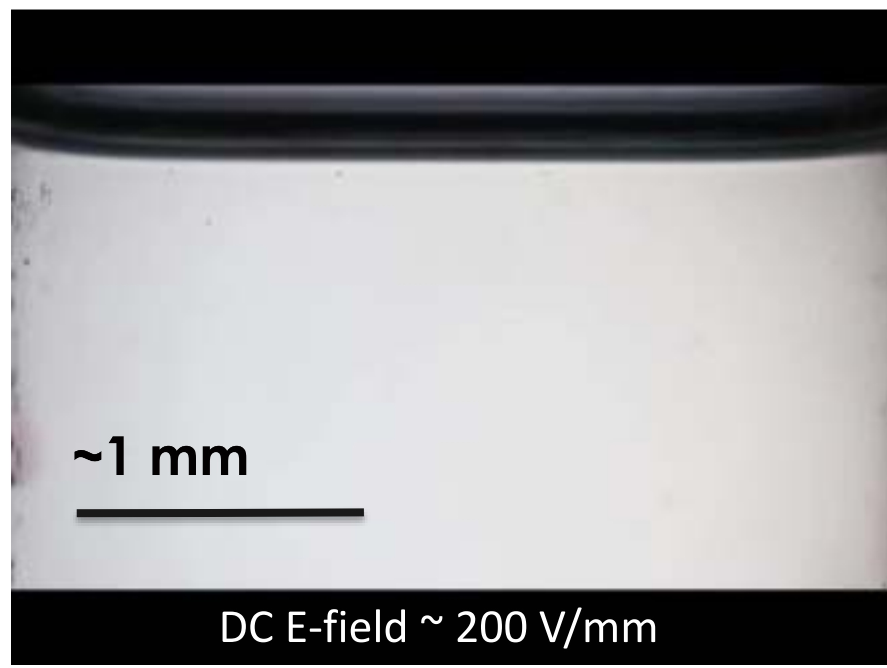


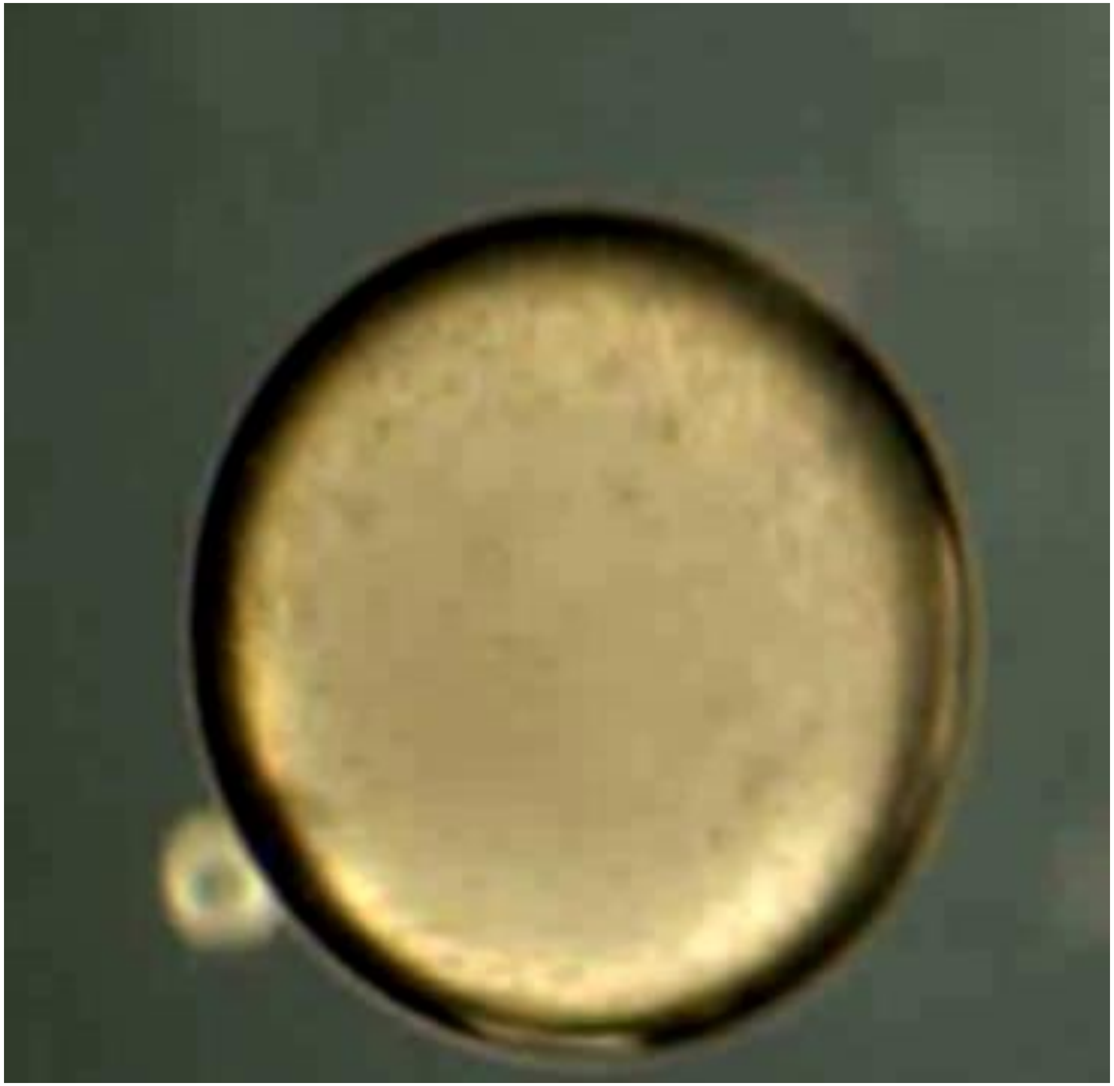
Clay in silicone oil dispersion

(~ 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.

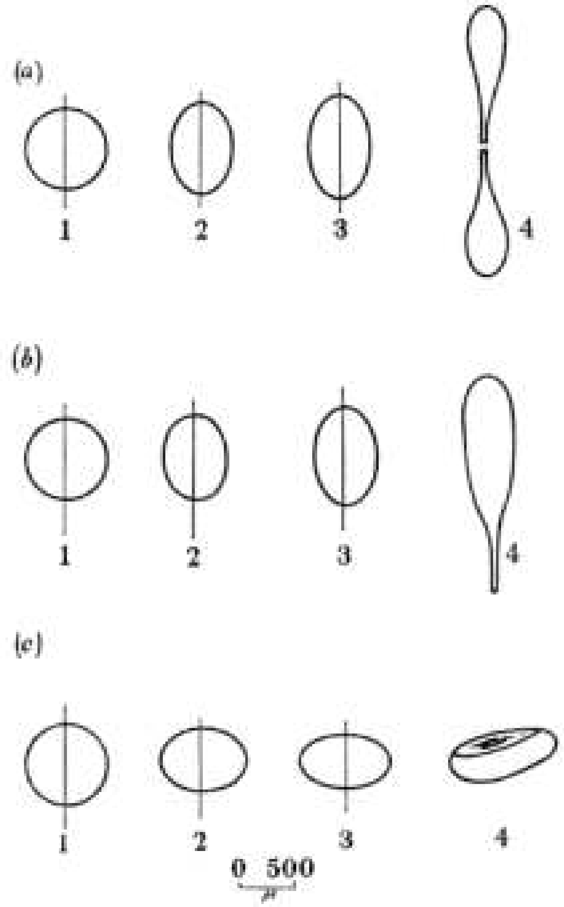


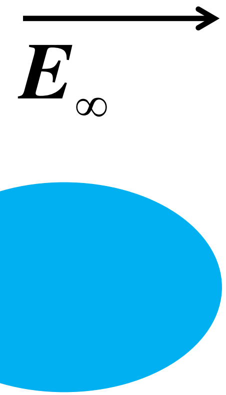
Figure 3. Tracings from typical photographs of drops in an electric field showing the change in D_e with increasing E_0 up to break-up. (a) $q = \infty$ (system 13). The drop in picture 4 separated into two halves with a large number of fine droplets in between at $(E_0^2 b) = 2{\cdot}9 \times 10^5\ \mathrm{V^2\,cm^{-1}}$. (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 $(E_0^2 b) = 3{\cdot}7 \times 10^5\ \mathrm{V^2\,cm^{-1}}$.

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

Fluid drops subject to a uniform electric DC field

Perfect dielectric drop:

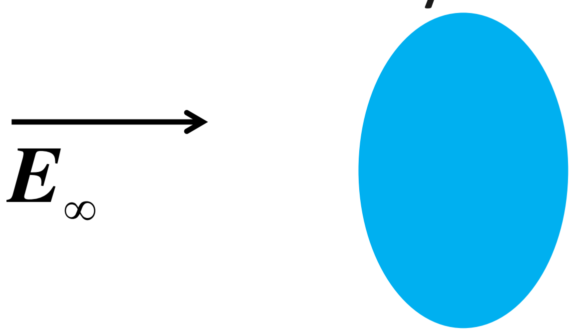
Drop deformation



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.

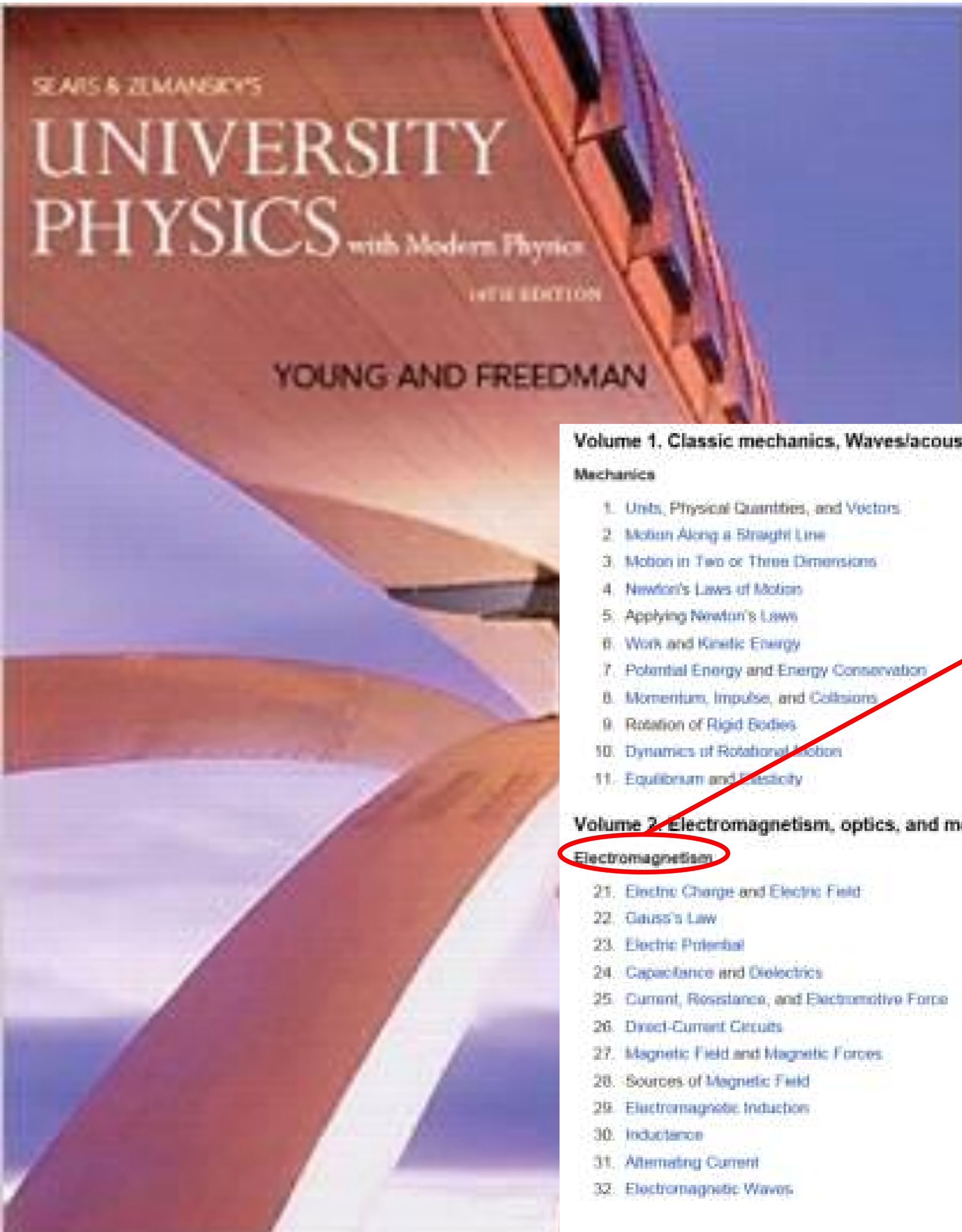
(*Received* 22 *July* 1965)

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

EHD

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

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

Maxwell-Wagner charge relaxation time

Ohmic conductor:

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

Maxwell (Gauss) equation:

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

Charge conservation:

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

Keep free charges

Exponential decay of free charges in bulk:

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

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

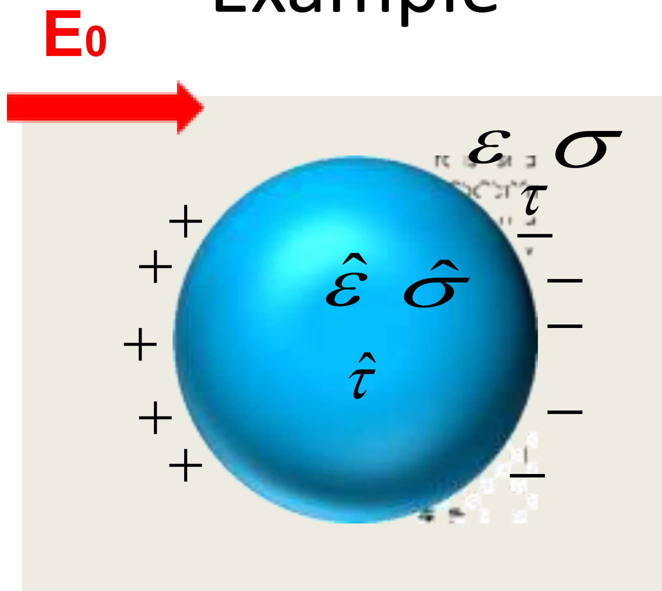
$$\tau_{MW} = \frac{\varepsilon}{\sigma}$$

Time it takes to reach electrical stationary state

Maxwell-Wagner time

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

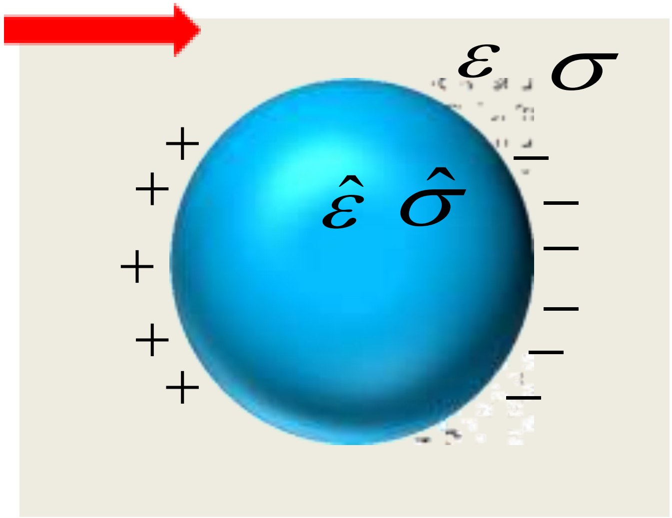
After about 1 second there are no free charges in bulk, only at boundaries

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

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

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

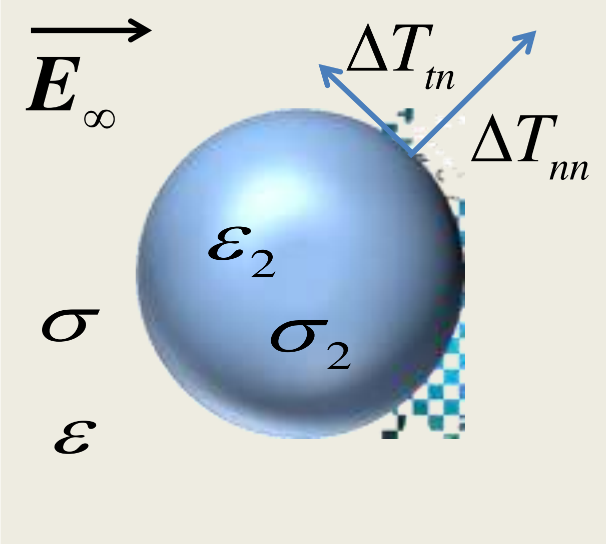
$$E_t = \hat{E}_t$$



Free charges on the droplet surface:

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

Conducting fluids



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

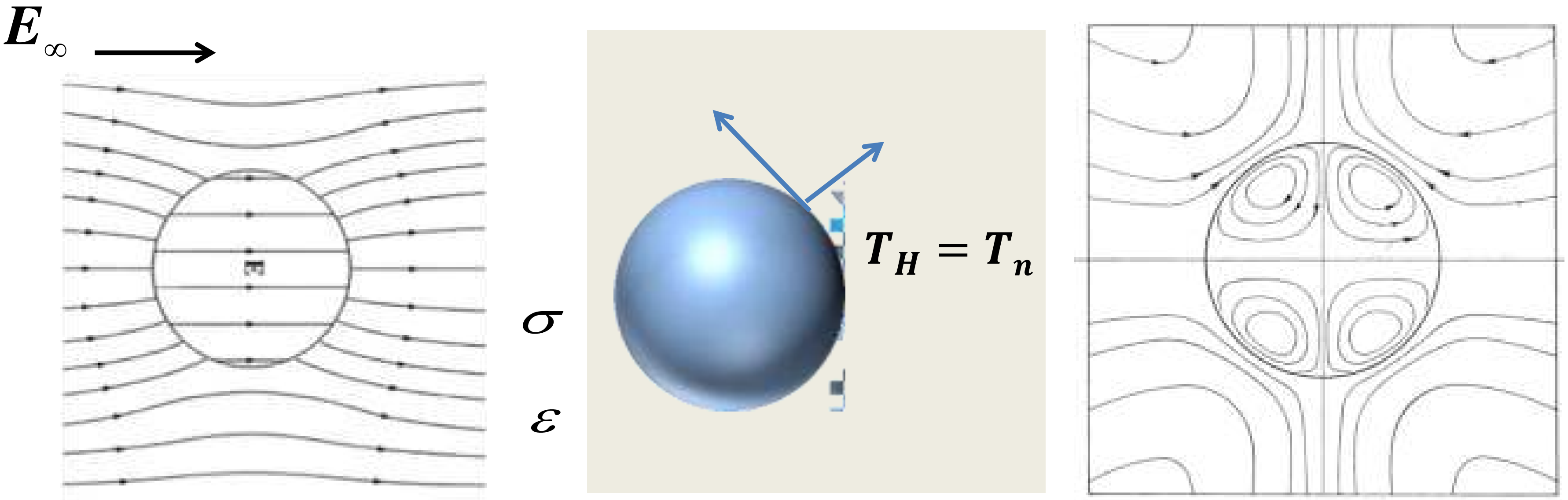
$$\Delta T_{tn} = (\varepsilon_1 E_{1n} - \varepsilon_2 E_{2n})E_t = \sigma_f E_t$$

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

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

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

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

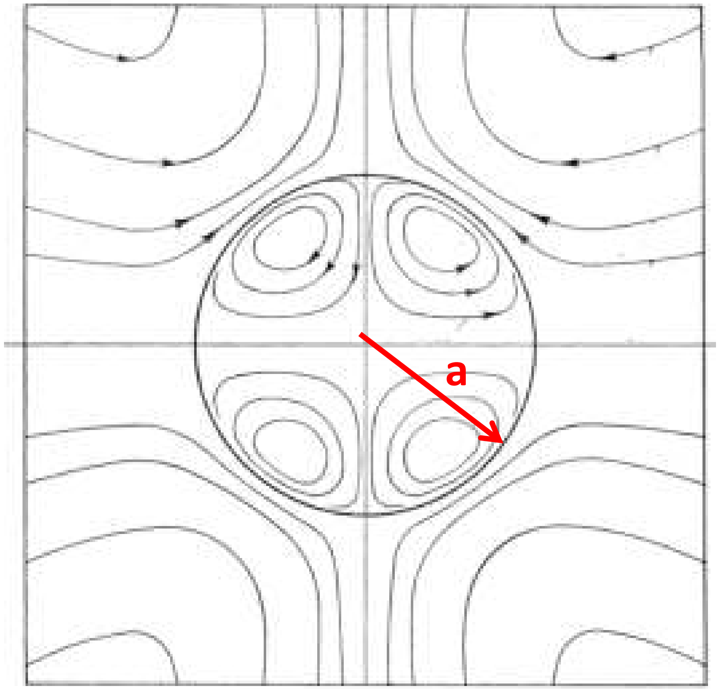
$$\mathbf{T}_{Maxwell} = \varepsilon\left(\boldsymbol{EE} - \frac{1}{2} E^2 \mathbf{I}\right)$$

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

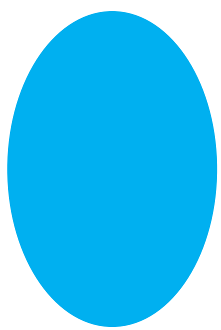
↓

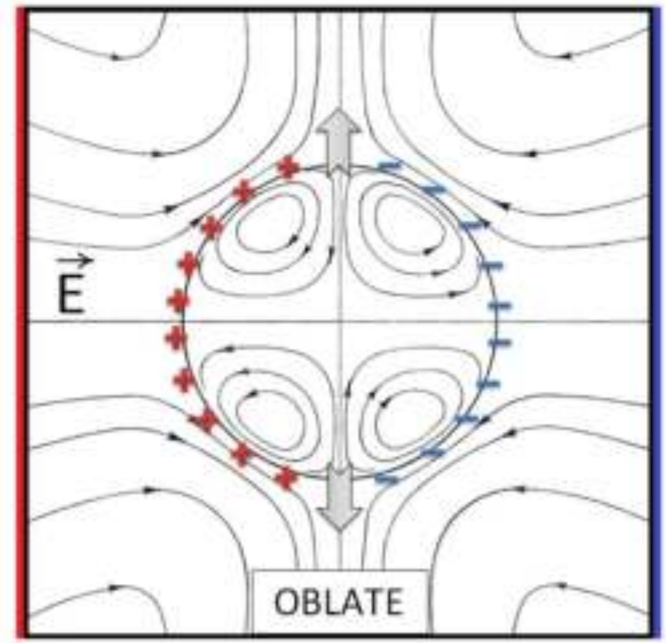
Maxwell electric stress

↓

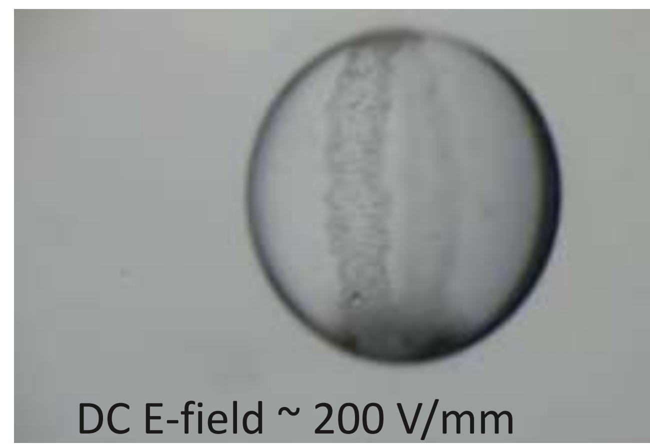
Liquid circulation flows

Oblate deformation





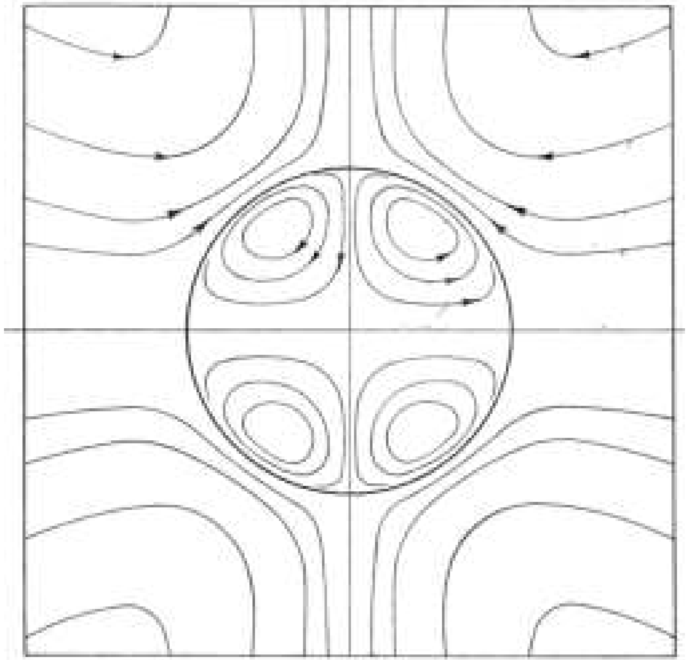
Ribbon structure

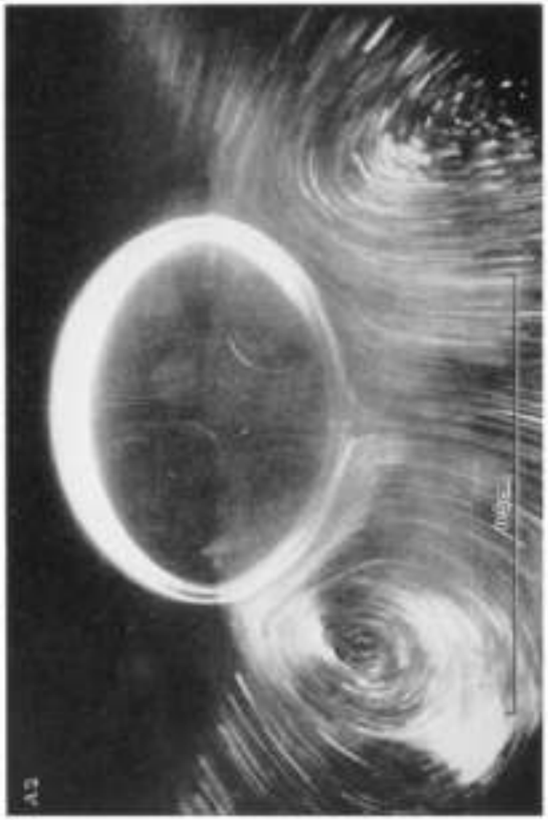


Electro-hydrodynamic Taylor flow

From Taylors original paper:

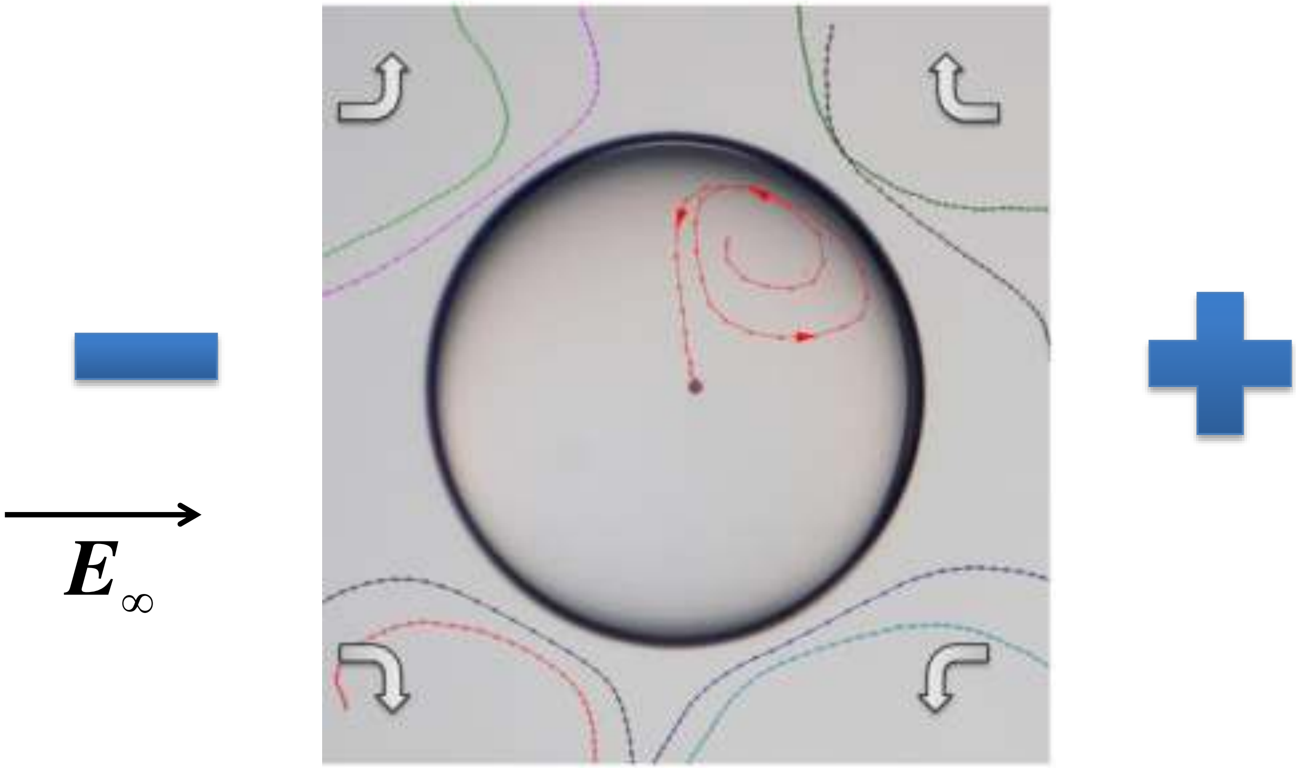
G.I. Taylor: Proc. R. Soc. Lond. A 291,159-166 (1966)





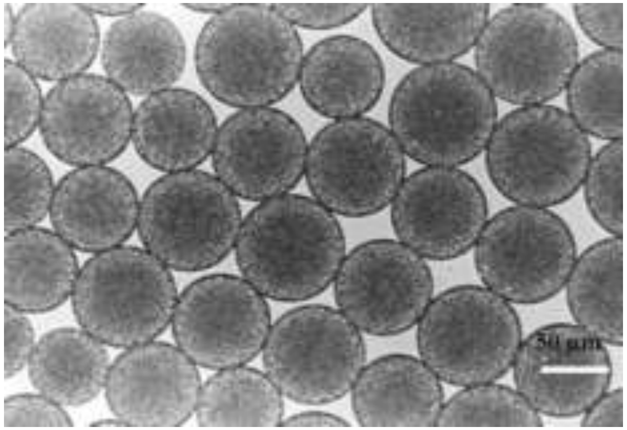
Conducting fluids

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.

Rhutesh K. Shah[a], Ho Cheung Shum[a], Amy C. Rowat[a], Daeyeon Lee[a], Jeremy J. Agresti[a], Andrew S. Utada[a], Liang-Yin Chu[a,b], Jin-Woong Kim[a,c], Alberto Fernandez-Nieves[a,d], Carlos J. Martinez[a,e], and David A. Weitz[a,f]*
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Monodisperse emulsions

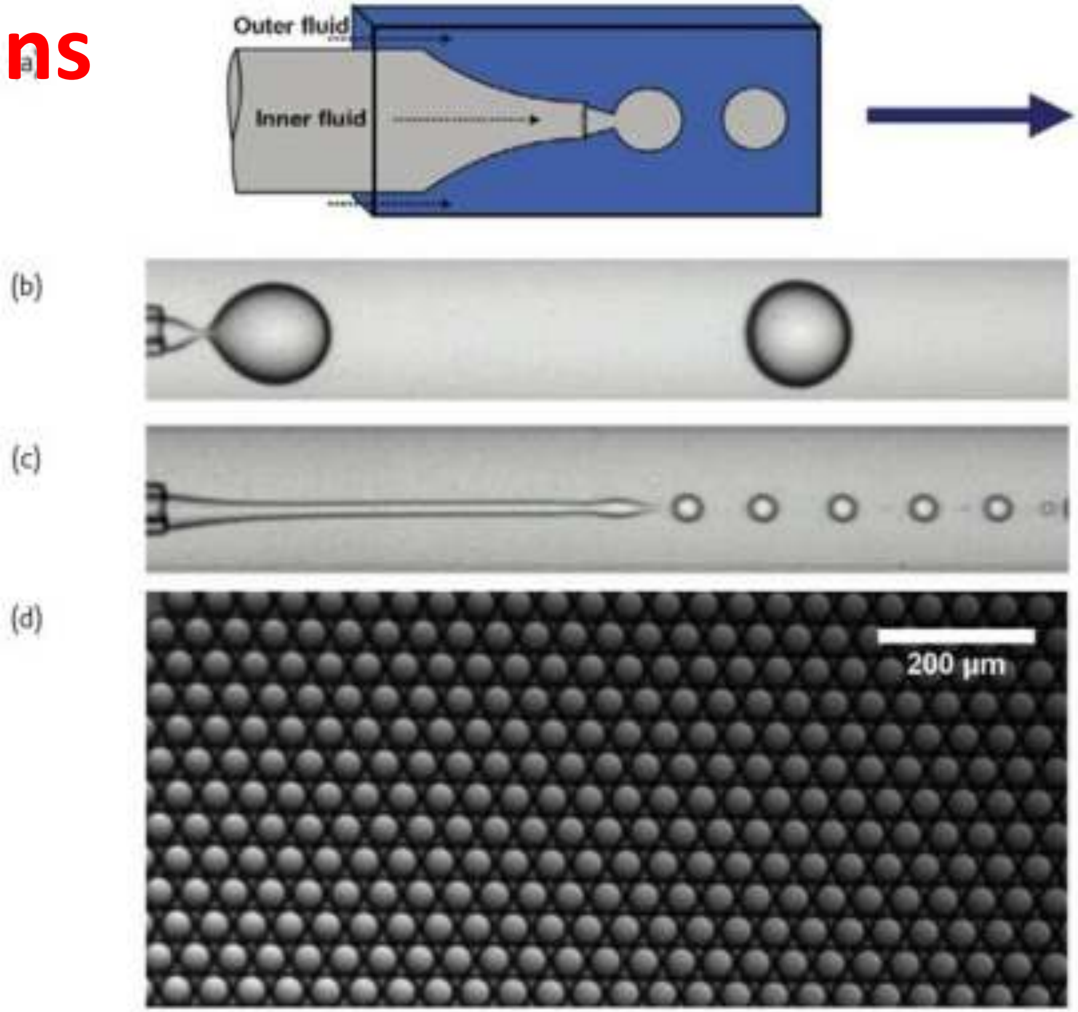
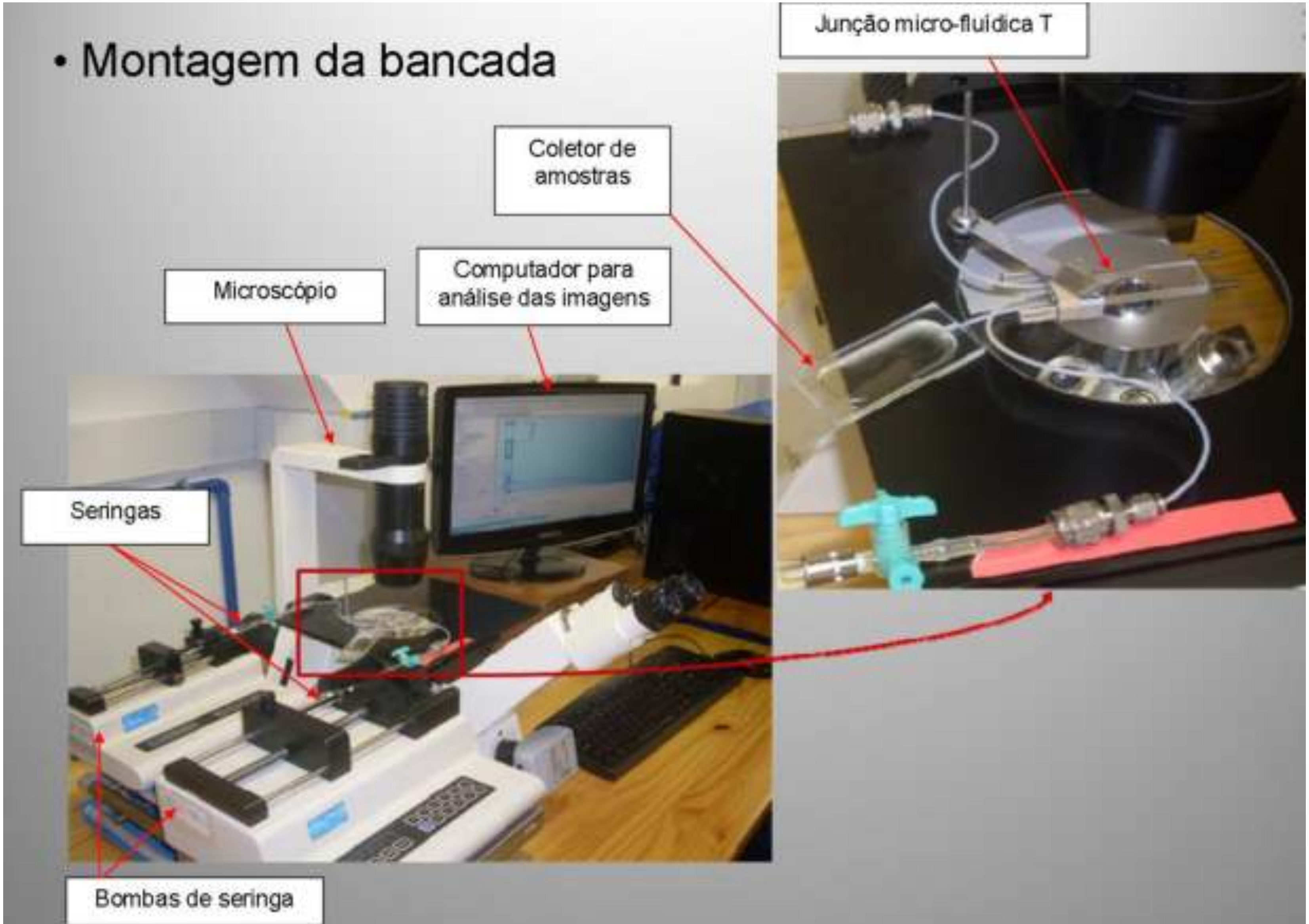


Fig. 2 Single emulsions in a co-flow microfluidic device. (a) Schematic of a co-flow microcapillary device for making droplets. Arrows indicate the flow direction of fluids and drops. (b) Image of drop formation at low flow rates (dripping regime). (c) Image of a narrowing jet generated by increasing 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:



CRITICAL REVIEW

Lab Chip, 2010, **10**, 2032–2045

Dynamics of microfluidic droplets

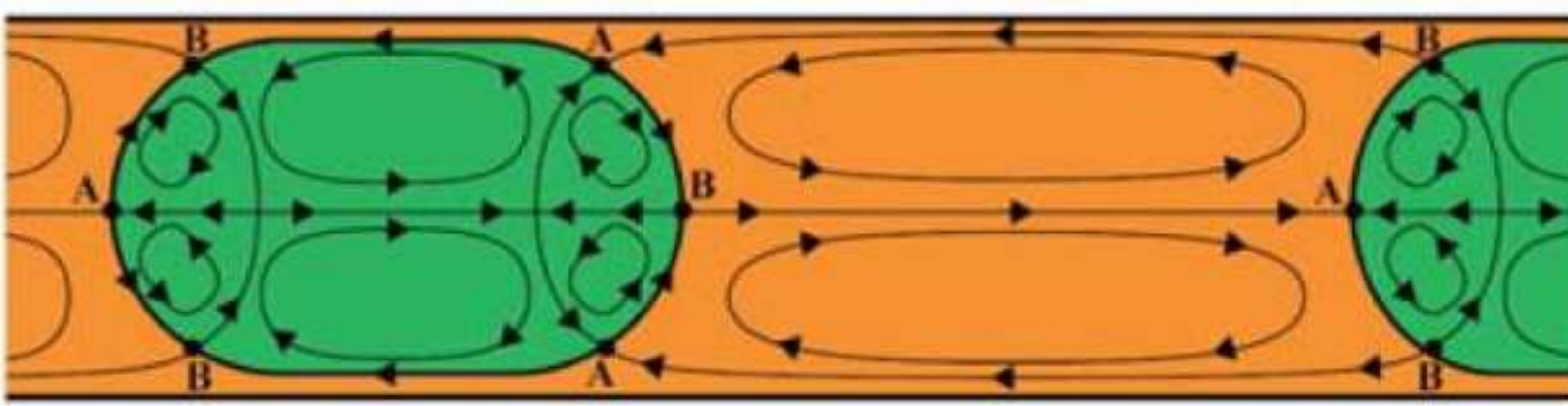
Charles N. Baroud,[*a] Francois Gallaire[b] and Rémi Dangla[a]

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 279
DOI: 10.1017/S0022112003007213 Printed in the United Kingdom

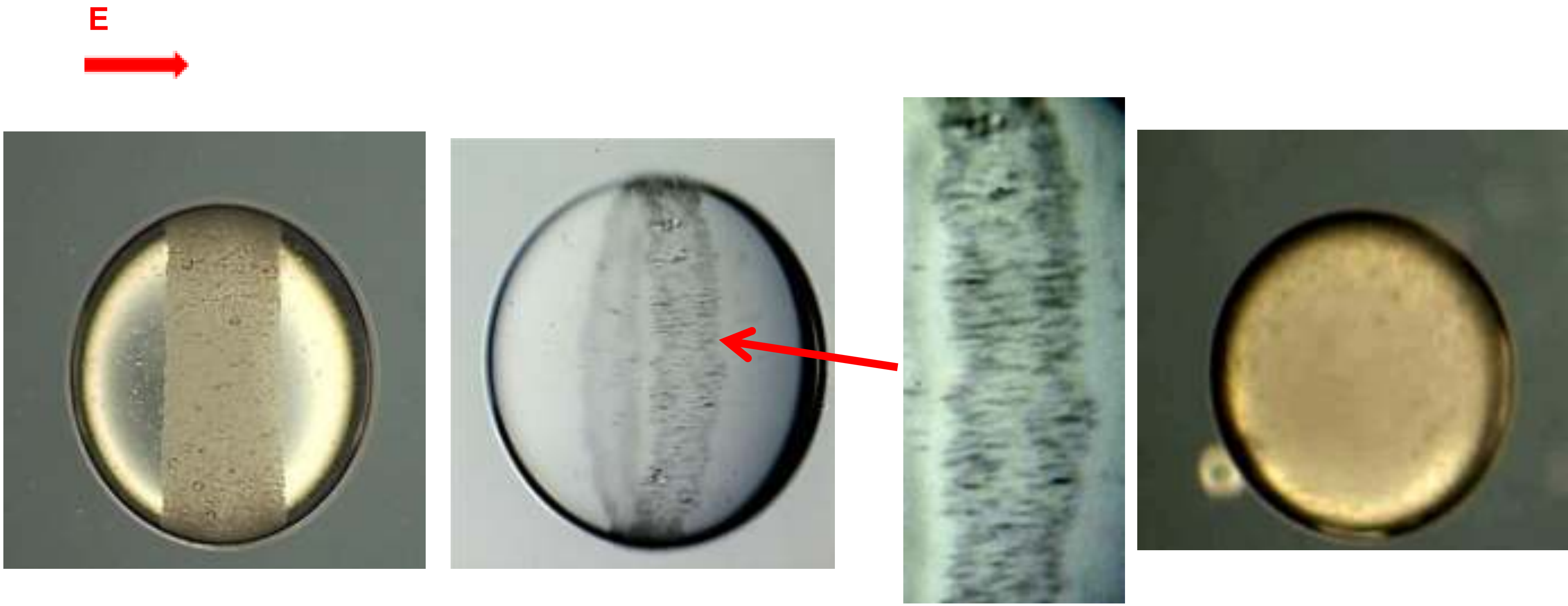
The motion of a viscous drop through a cylindrical tube

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

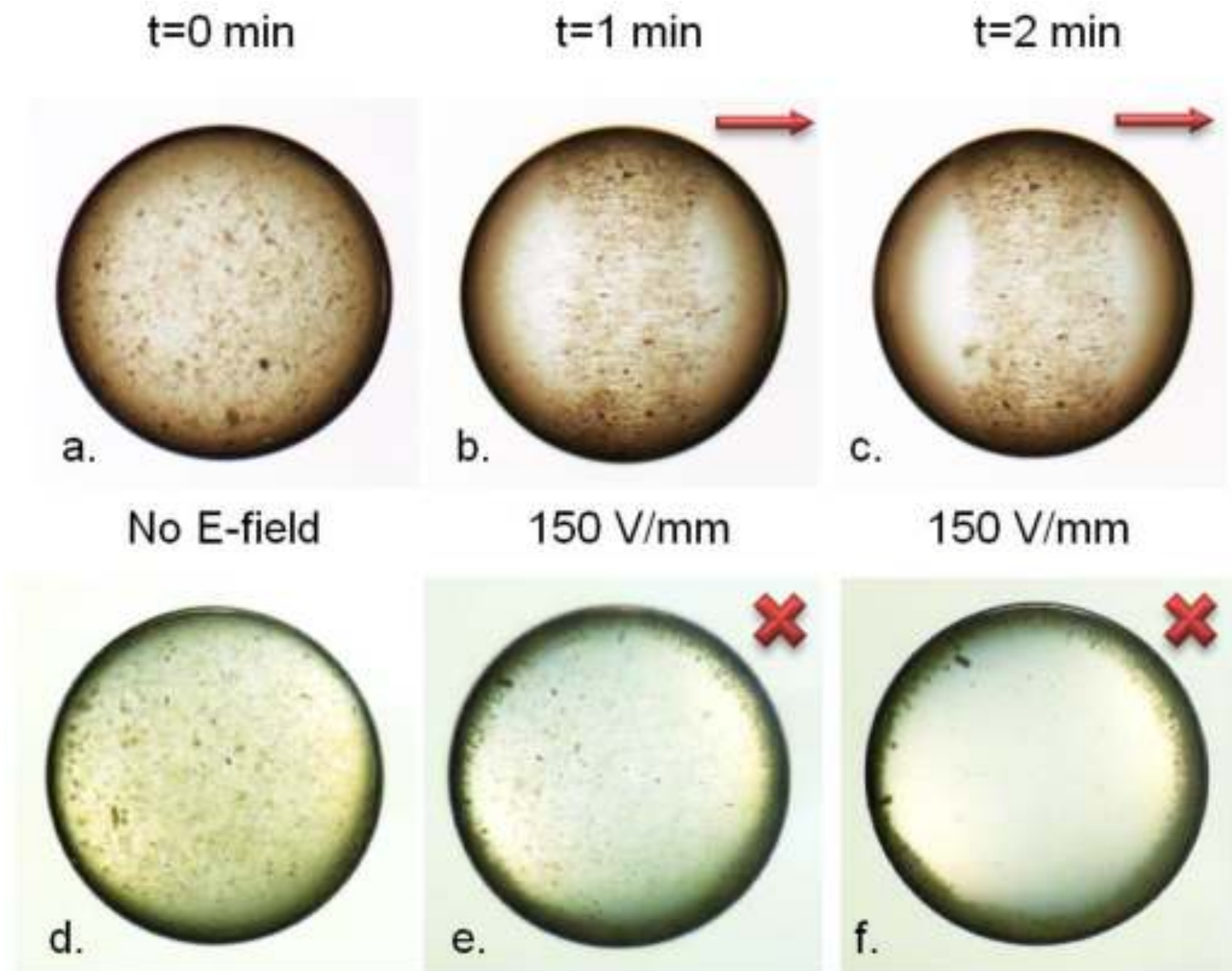


for low viscosity ratio

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

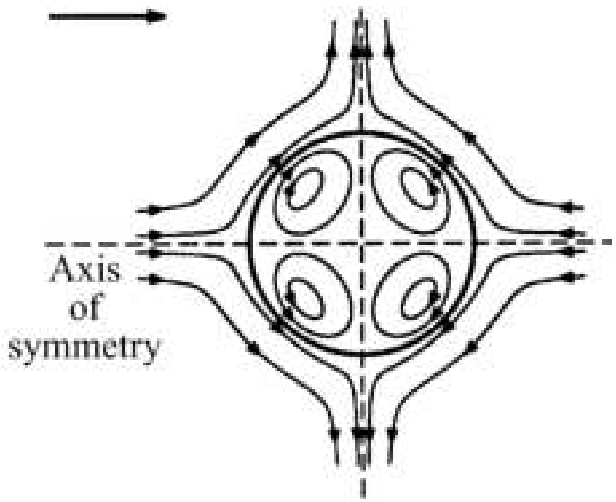


Ribbon-like structure: Experiments at NTNU Trondheim

Maxwell times determines direction of flow

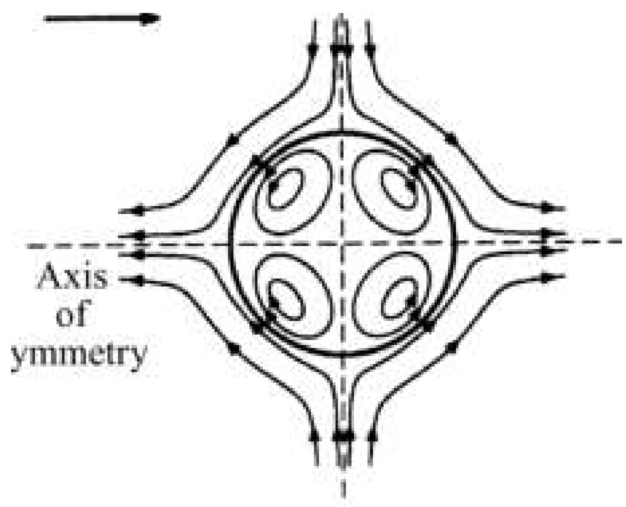
$$v_\theta = -\frac{9}{40\pi(\eta+\hat{\eta})}\frac{a\hat{\varepsilon}E^2}{\left(2+\frac{\hat{\sigma}}{\sigma}\right)^2}\left(\frac{\tau}{\hat{\tau}}-1\right)\cos 2\theta$$

$\hat{\tau} > \tau$



Flow towards equator

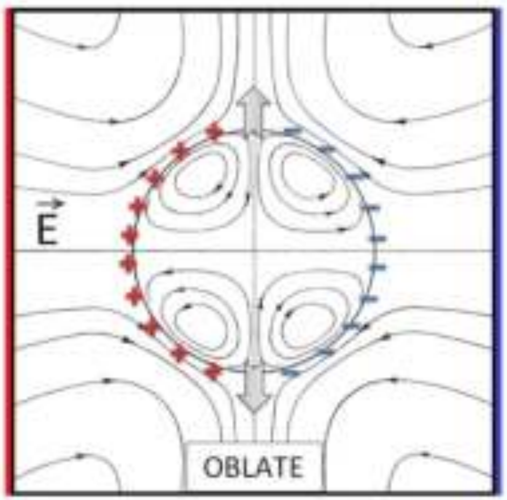
$\hat{\tau} < \tau$



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 <u>**electrical poles**</u> rather than to the electrical equator

Colloidal caps

Drop fluid

Electro-hydrodynamic flow

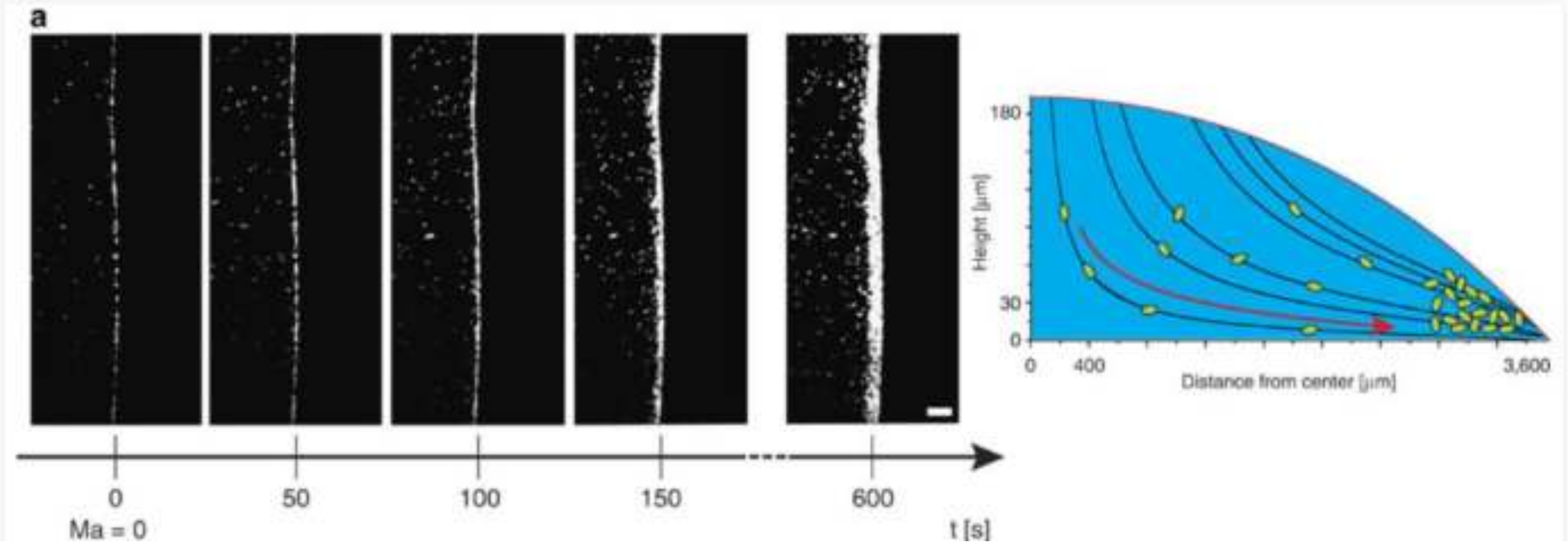
Coffe ring effect:
Convective deposition by hydrodynamic flow
(No direct electrical forces on particles)

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

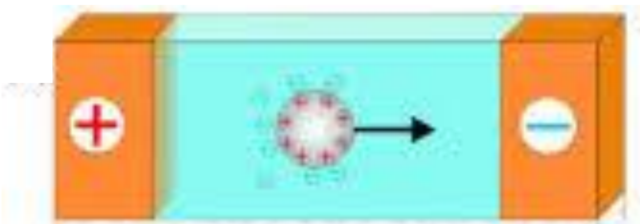
Nature Communications 4, Article number: 1757 | doi:10.1038/ncomms2746



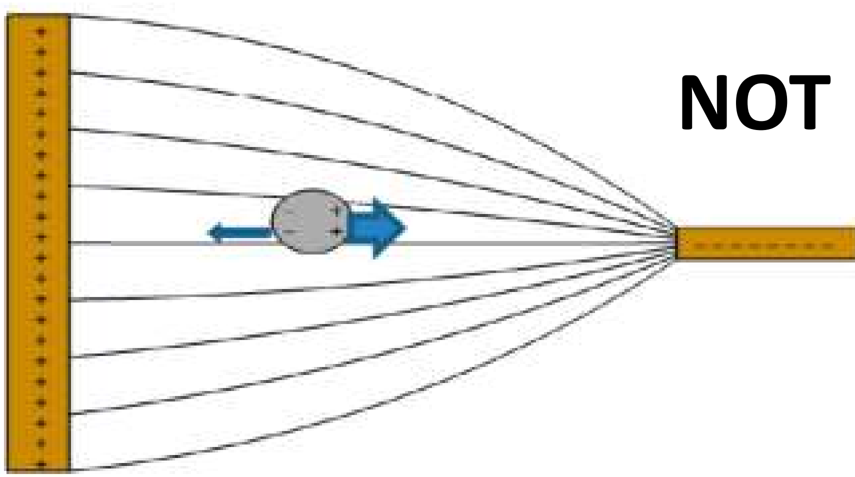
R. D. Deegan, O. Bakajin, T. F. Dupont, G. Huber, S. R. Nagel, T. A. Witten (1997). "Capillary flow as the cause of ring stains from dried liquid drops". *Nature* **389** (6653): 827–829

There are weak direct electrical forces on our particles

Convective deposition dominates here:

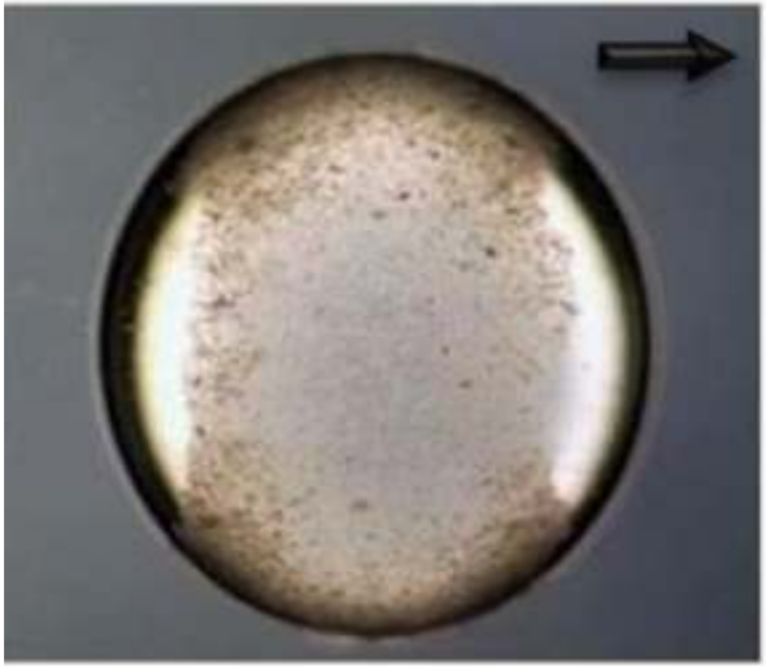


NOT Electrophoresis



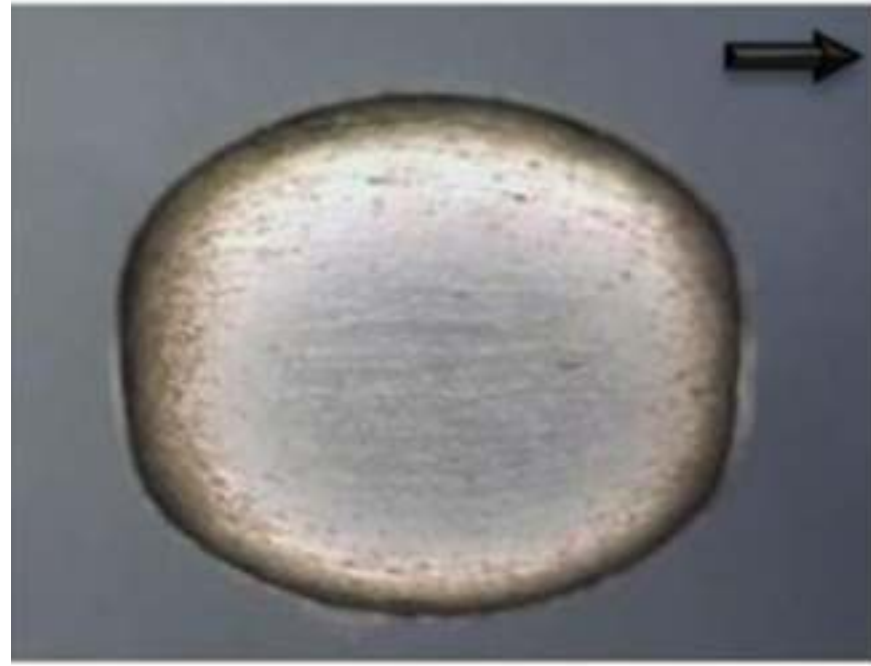
NOT Dielectrophoresis

Oblate-to-Prolate transition



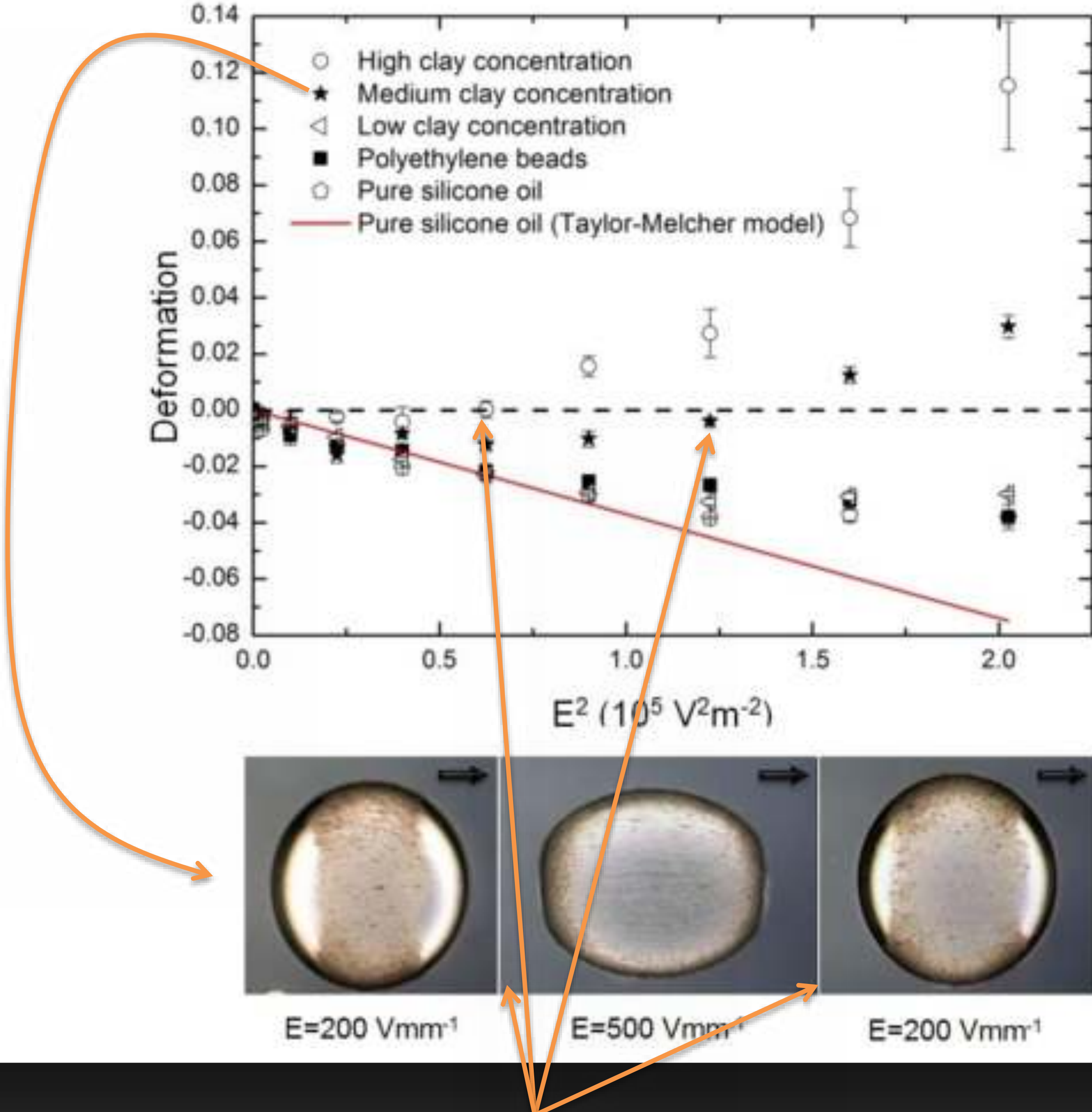
$E=200\ Vmm^{-1}$

Electro-hydrodynamic flow



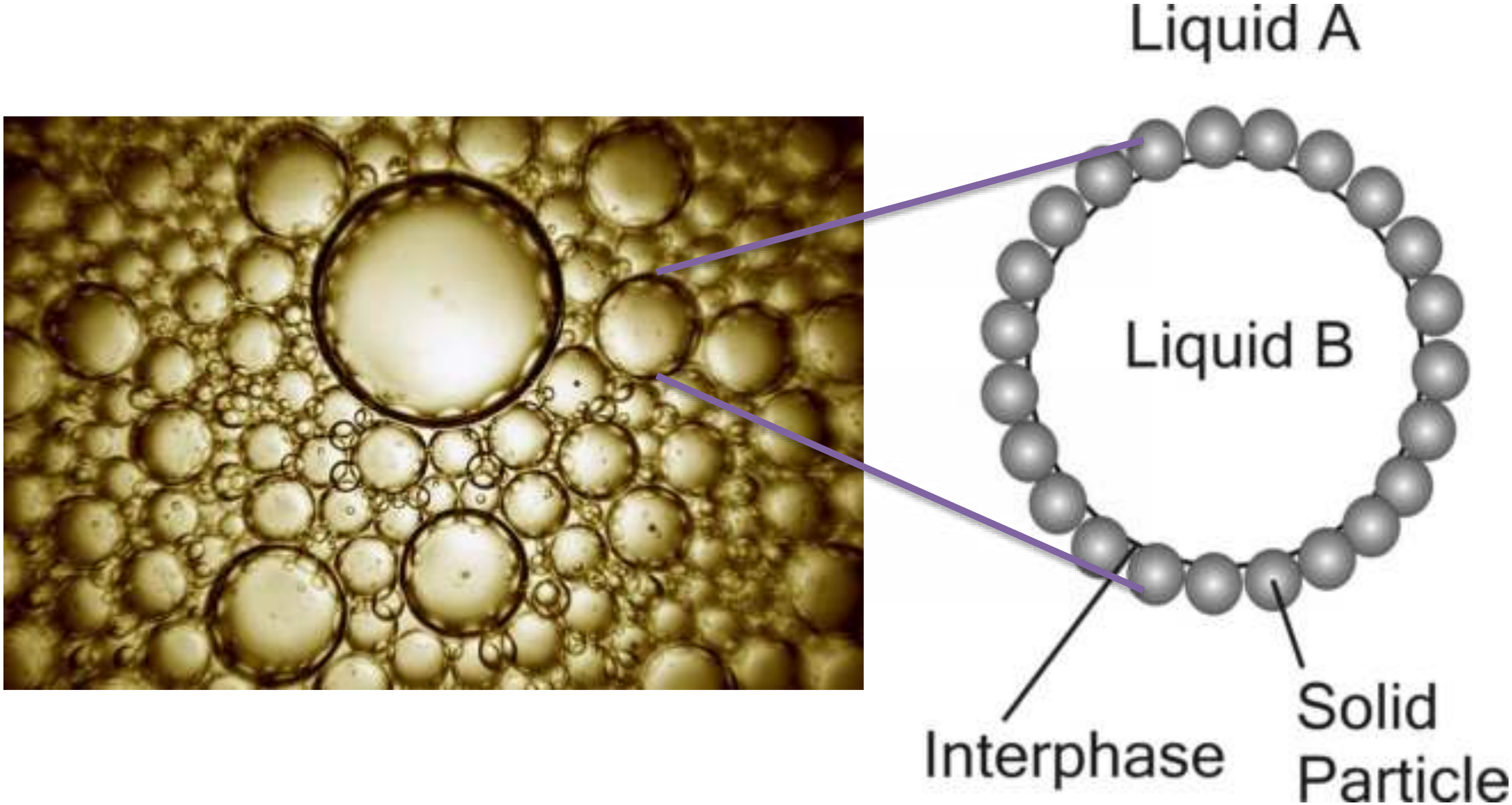
$E=500\ Vmm^{-1}$

Dipole-dipole interactions



Oblate-to-Prolate transition

Pickering («physical») emulsions



"Separation of Solids in the Surface-layers of Solutions and 'Suspensions' (Observations on Surface-membranes, Bubbles, Emulsions, and Mechanical Coagulation). — Preliminary Account." By W. RAMSDEN, M.A., M.D., Oxon., Fellow of Pembroke College, Oxford. Communicated by Professor F. GOTCH, F.R.S. Received June 8,—Read June 18, 1903.

J. Chem. Soc., Trans., 1907,**91**, 2001-2021

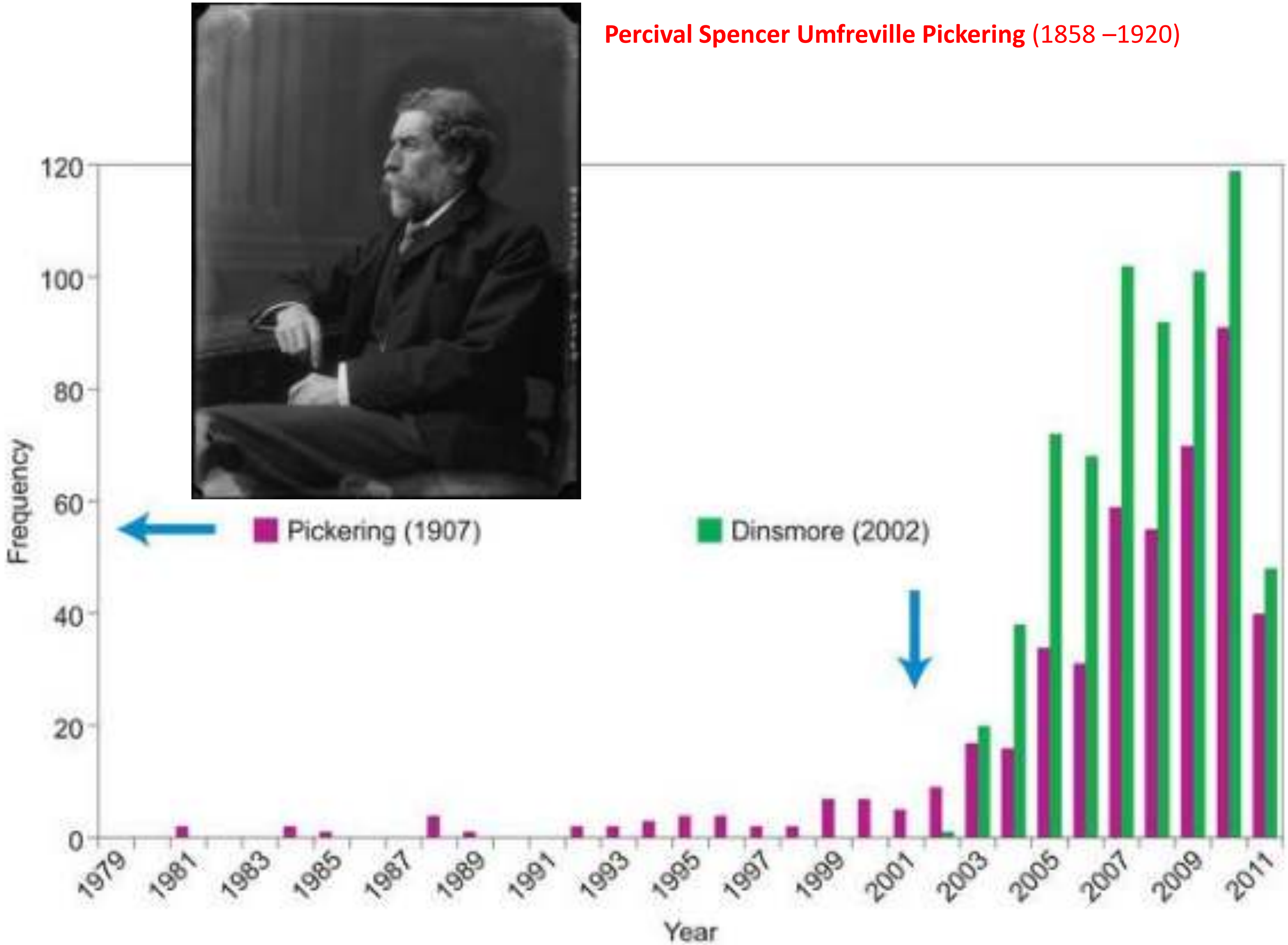
CXCVI.—*Emulsions.*

By SPENCER UMFREVILLE PICKERING, M.A., F.R.S.

IN the Sixth Report of the Woburn Experimental Fruit Farm (Eyre and Spottiswoode, 1906) were published the results of an examination of emulsions of paraffin oil in solutions of soft soap, such as are used for insecticidal purposes; this examination has now been extended with the double object of obtaining an emulsifying agent which would, for practical purposes, not be open to the objections presented by those containing soap, and also of elucidating the nature of emulsification. The subject had already been investigated by Ramsden (*Proc. Roy. Soc.*, 1903, **72**, 156), but his work, unfortunately, did not come under the notice of the writer until that here described had been completed. It is satisfactory to find, however, that Ramsden, pursuing a different line of enquiry, should have arrived at an explanation of emulsification which is essentially the same as that given here.

Percival Spencer Umfreville Pickering (1858 –1920)

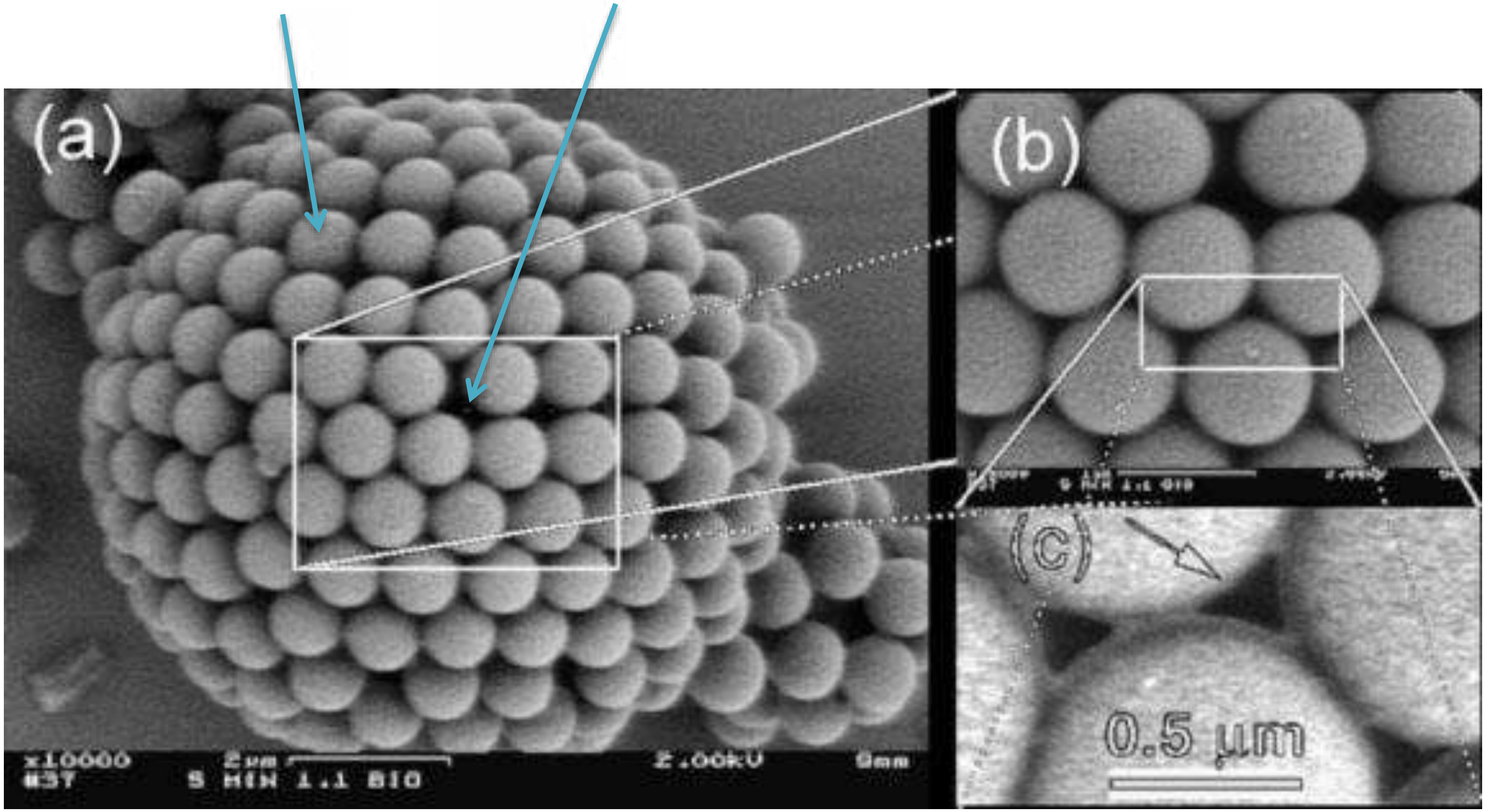
Percival Spencer Umfreville Pickering (1858 –1920)



Lost history versus good science, Qian Wang, & Chris Toumey, Nature Chemistry 3, 832–833, doi:10.1038/nchem.1179 (2011)

Colloidosomes

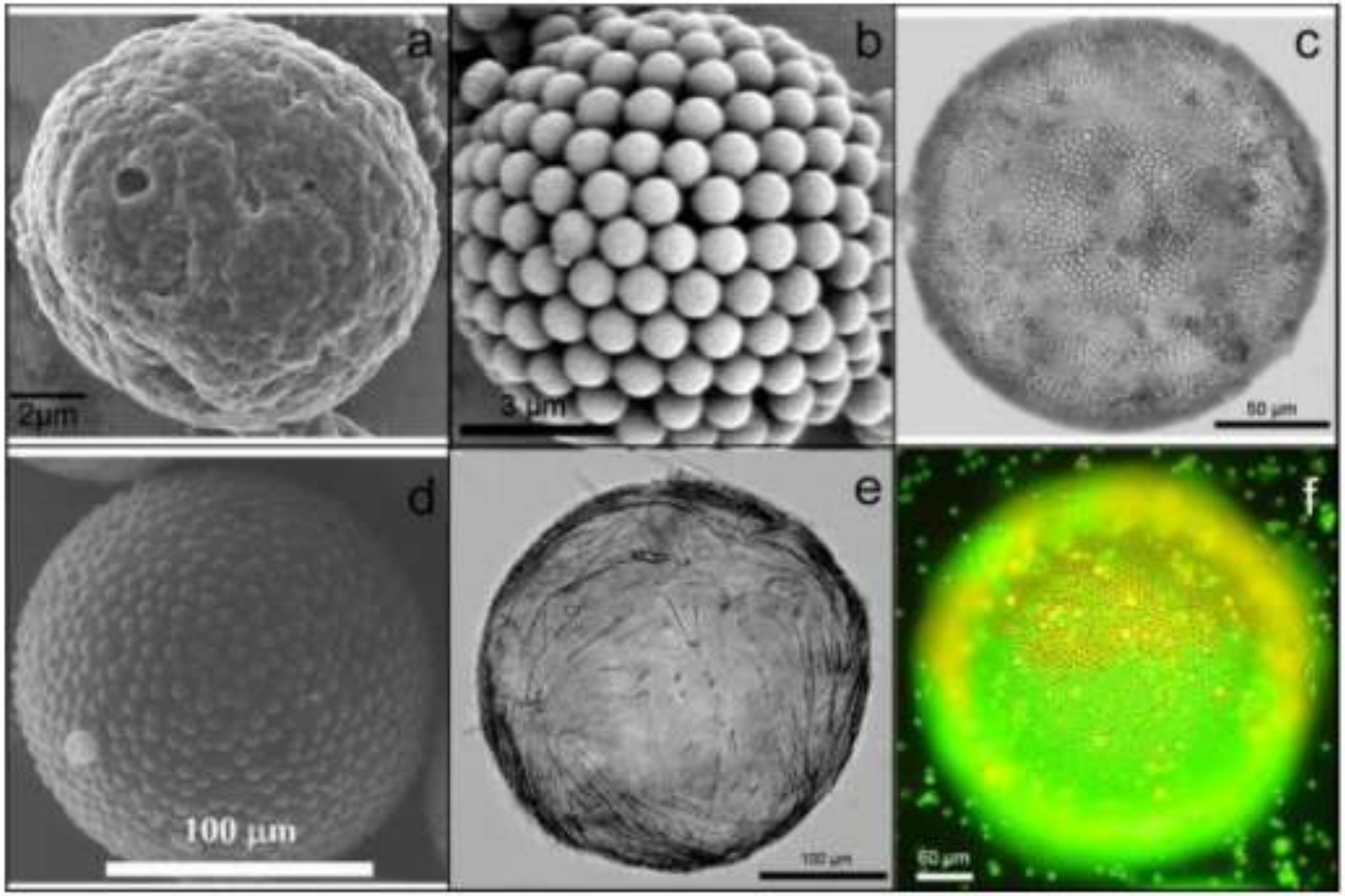
Composition and permeability



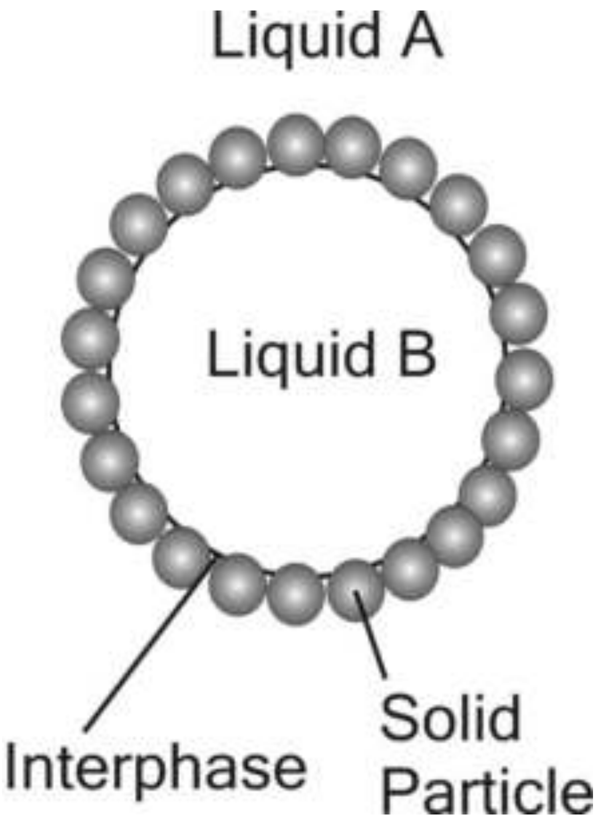
A.D. Dinsmore et. Al., Science, **298**, 1006 (2002); David Weitz group: Harvard Univ.

Pickering (1907) : Emulsions

Dinsmore et al. Science (2002): "Colloidosomes"



Dinsmore et.al.



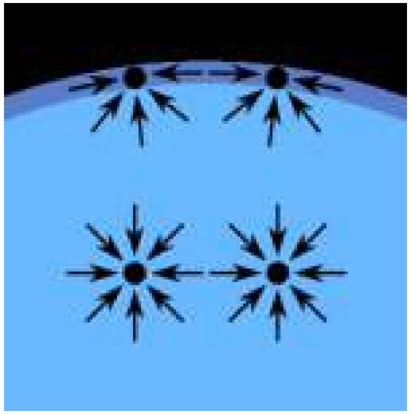
Surface Energy: $E = \gamma A$

$A = \text{Surface area}$ $\gamma_{WA} = 0.0073\,\text{N/m}$

Capillary binding: A particle at the interface is trapped in a capillary barrier with a substantial energy cost of moving to either side of the liquid interface.

Origin of capillary binding:
Surface tension:

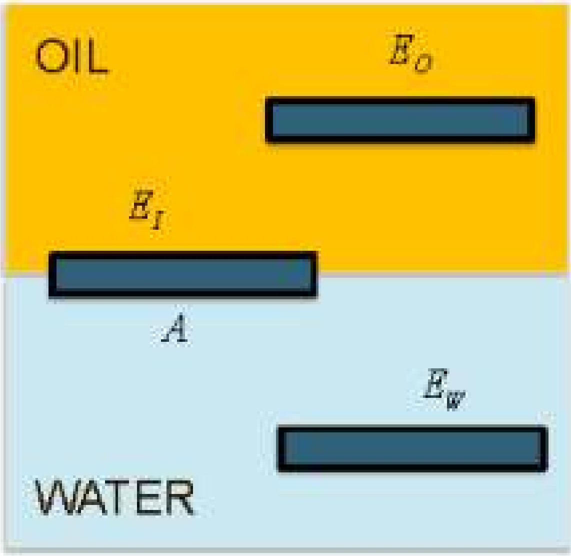
The forces on molecules of a liquid:



Surface tension preventing a paper clip from submerging

Capillary binding

Capillary binding of a <u>flat</u> solid particle at a liquid interface



Particle surface energy :

$$E_O = 2A\gamma_{SO}$$

$$E_W = 2A\gamma_{SW}$$

$$E_I = A\gamma_{SO} + A\gamma_{SW} - A\gamma_{OW}$$

Energy gain :

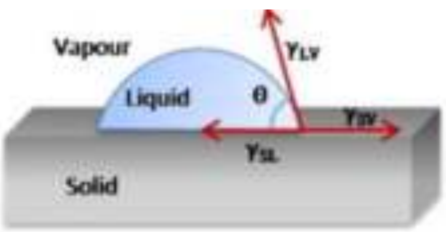
$$E_I - E_O = -A\gamma_{OW}(1 + \cos\theta)$$

$$E_I - E_W = -A\gamma_{OW}(1 - \cos\theta)$$

Wetting angle Young's relation:

$$\gamma_{SO} = \gamma_{SW} + \gamma_{OW}\cos\theta$$

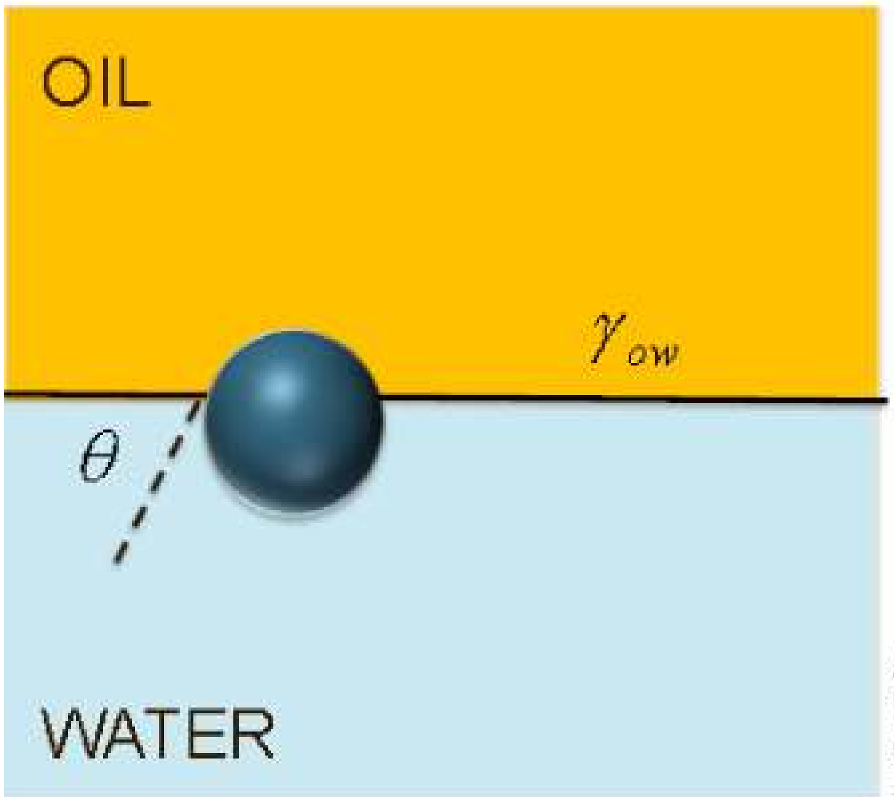
Energetically favorable to adsorb particles at the interface.



Typically:

$A_p\gamma_{OW}$ ~ 10000 kT for microparticles

Capillary binding of a bead is similar



Energy gain :

$$\Delta E = \pi r^2 \gamma_{ow} (1 \pm \cos\theta)^2$$

Adsorption Energy of Nano- and Microparticles at Liquid–Liquid Interfaces

Kan Du †, Elizabeth Glogowski ‡§, Todd Emrick ‡, Thomas P. Russell *‡ and Anthony D. Dinsmore *†
† Physics Department
‡ Polymer Science and Engineering Department
University of Massachusetts, Amherst, Massachusetts 01003
§ Department of Chemistry, University of Illinois at Urbana–Champaign, Urbana, Illinois 61801

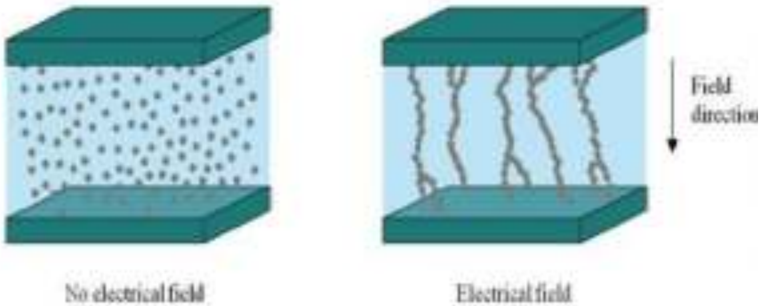
Langmuir, **2010**, 26 (15), pp 12518–12522
DOI: 10.1021/la100497h
Publication Date (Web): July 1, 2010

Typically:

$A_p \gamma_{OW}$ ~ 10000 kT for microparticles

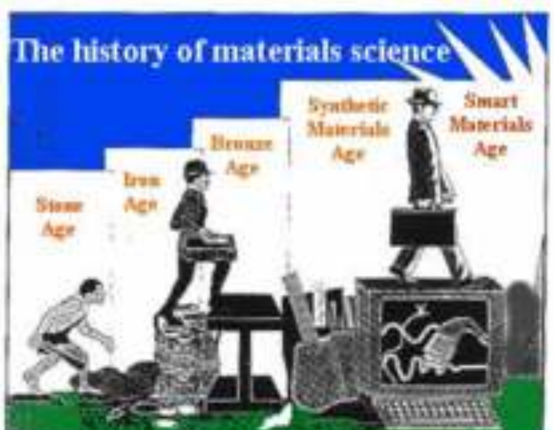
Electro-rheological fluids

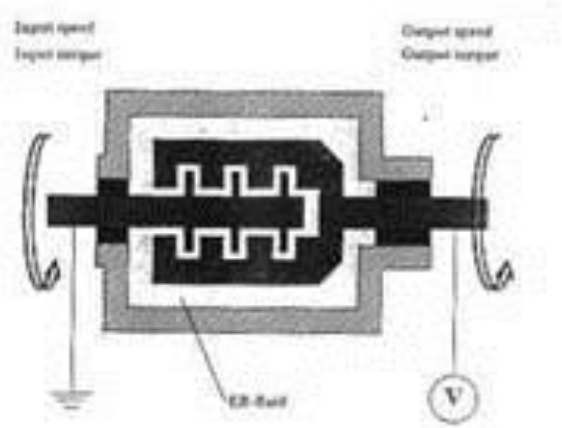
Winslow effect:



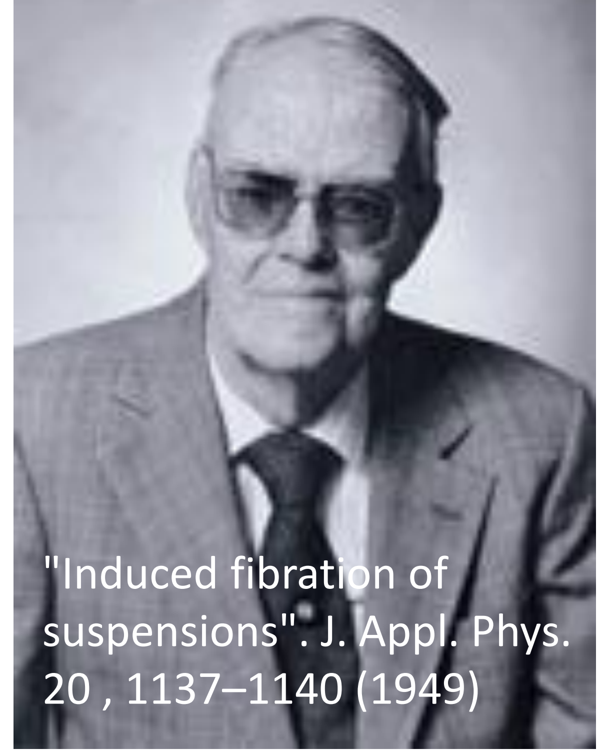
Viscosity can increase by a factor 100 000 in response to an electric field!

- Electric fields induce dipole attraction and chain formation
- Large yield stress -> 200 kPa or more 100 times viscosity increase (up to 100000 times according to wiki)





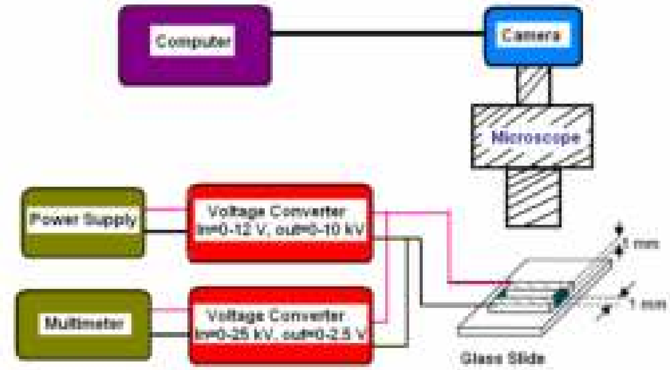
Winslow, Willis M.



"Induced fibration of suspensions". J. Appl. Phys. 20 , 1137–1140 (1949)

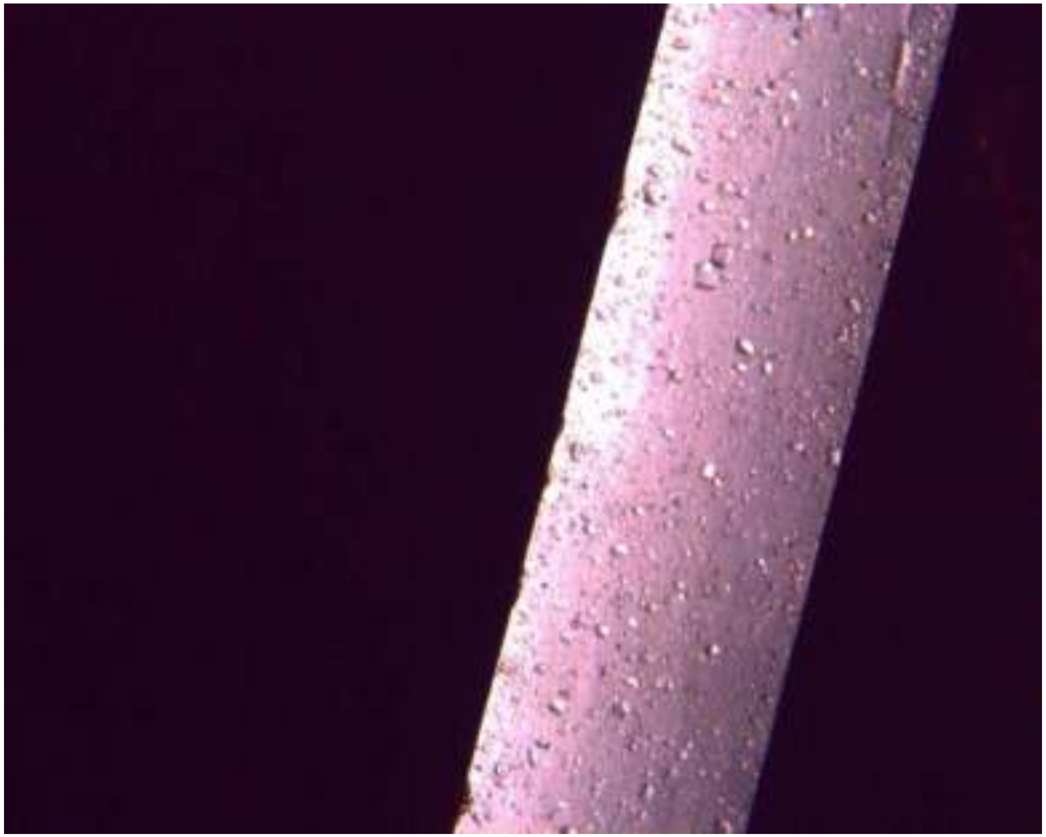
U.S. Patent 2,417,850: Winslow, W. M.: 'Method and means for translating electrical impulses into mechanical force', 25 March 1947

Clay particles suspended in oil:

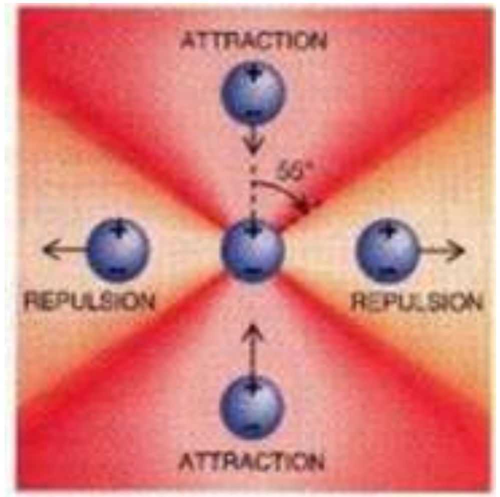


Video microscopy (real time):

~500 V



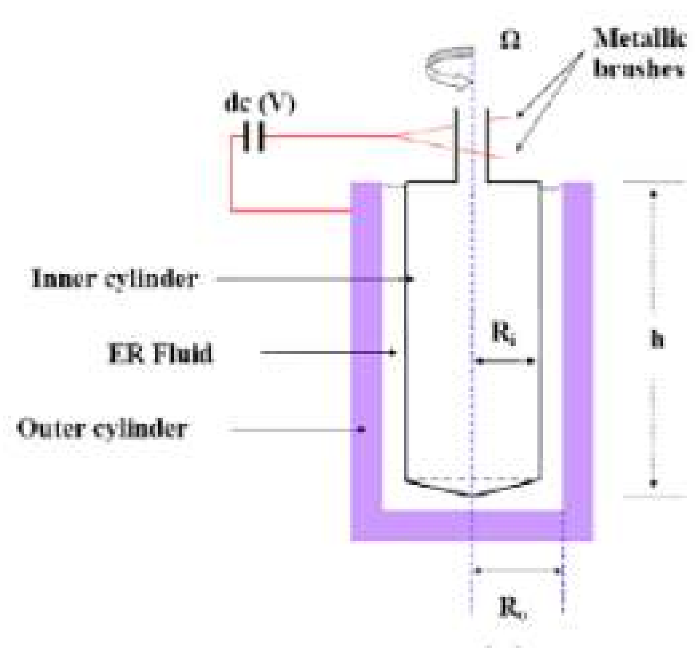
1 mm



Electrorheology: Smart Materials

Intercalation-enhanced electric polarization and chain formation of nano-layered particles, J.O. Fossum, Y. Méheust, K.P.S. Parmar, K.D. Knudsen, K.J. Måløy and D. M. de Fonseca, Europhys. Lett., 74, 438-444 (2006)

Our Physica MCR 300 Rheometer inl electrorheol. cell:



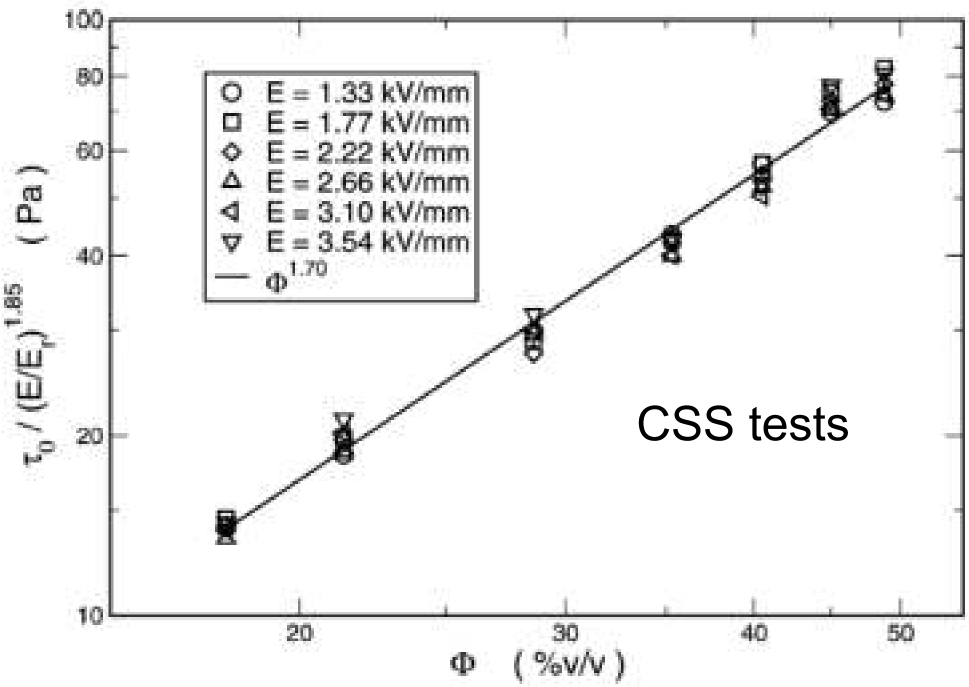
Langmuir 24, 1814 (2008)

J. Phys.: Condens. Matter 22, 324104 (2010)

J. Rheol. 55, 2011 (2010)

Yield stress:

Theories predict: $$\tau \propto E^{\alpha}\,\Phi^{\beta}$$



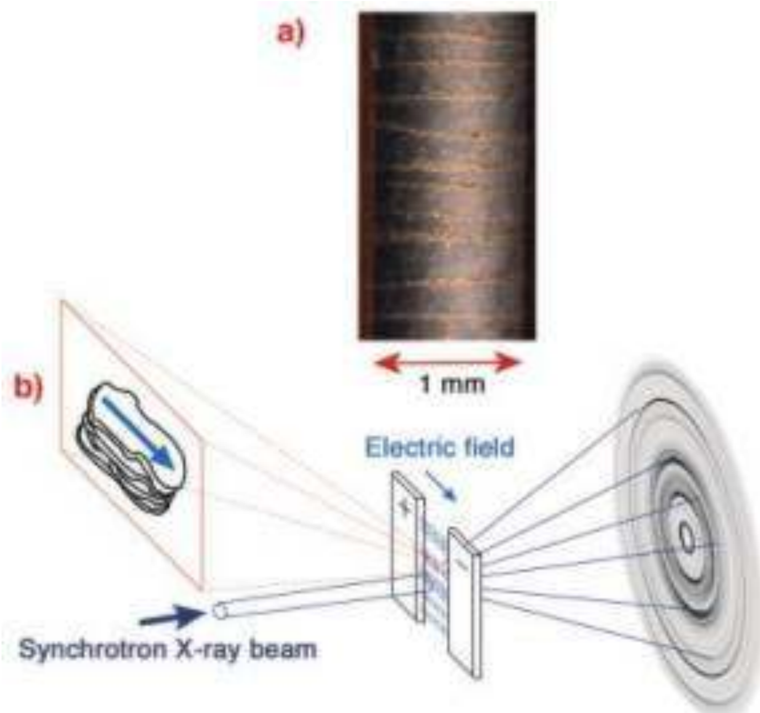
Static yield stress:
Yield stress for an undisrupted ER fluid.

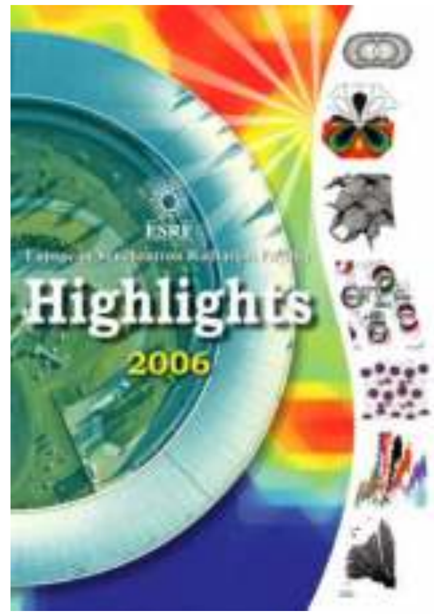
Log-log plot of the static yield stress, normalized by $E^{1.86}$, vs. the volume fraction at different strengths of the applied electric field. A power law $\beta \approx 1.70$ fits to the whole dataset..

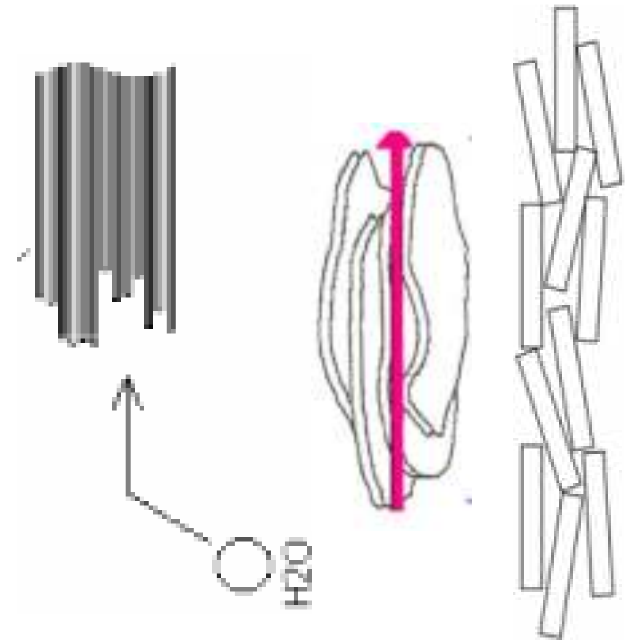
Table 1. Comparison of Static Yield Stress Values for Various ER Fluids Including That Addressed in the Present Paper, under an Applied Electric Field of About 1.0 kV/mm

ER fluids →	our sample	mica[18]	hematite[43]	saponite[44]	zeolite[45]	GER[46]
Φ →	1.9% (v/v)	15% (v/v)	15% (v/v)	0.11 g/mL	30% (v/v)	30% (v/v)
τ_0 (Pa) →	~20	~100	~85	~50	~3000	~15000

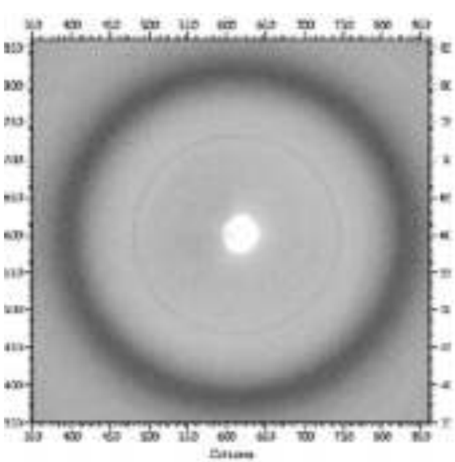
Experiments at ESRF, Grenoble:
In ESRF Scientific Highlights 2006



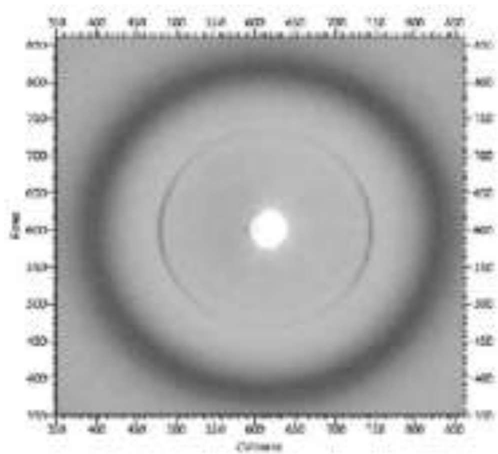


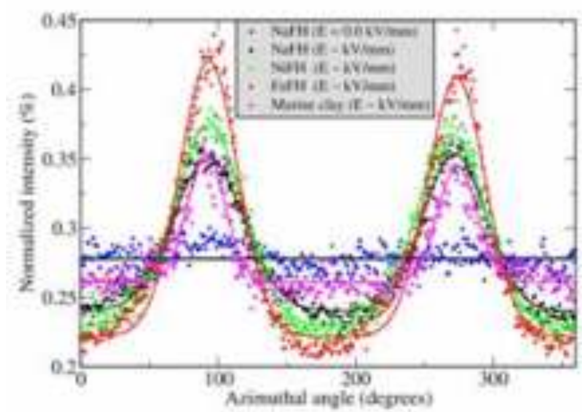


Before: 0 V/mm

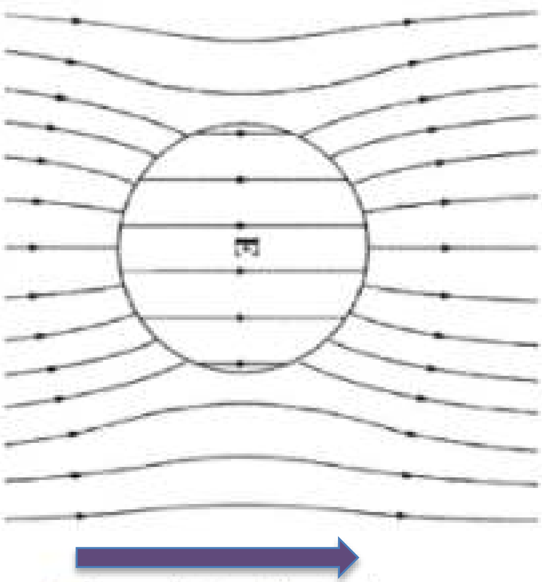


After: 500 V/mm

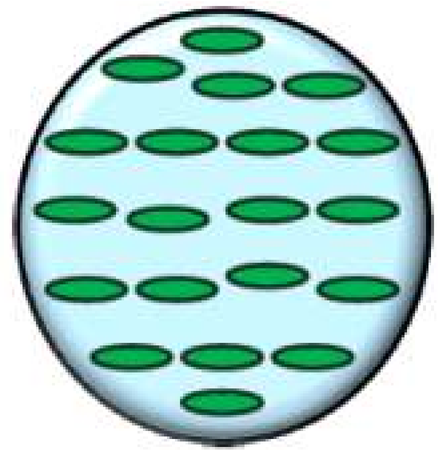




Angular distribution function $= S_2 = \frac{1}{2}\langle 3\cos^2\theta - 1\rangle$



Electric field



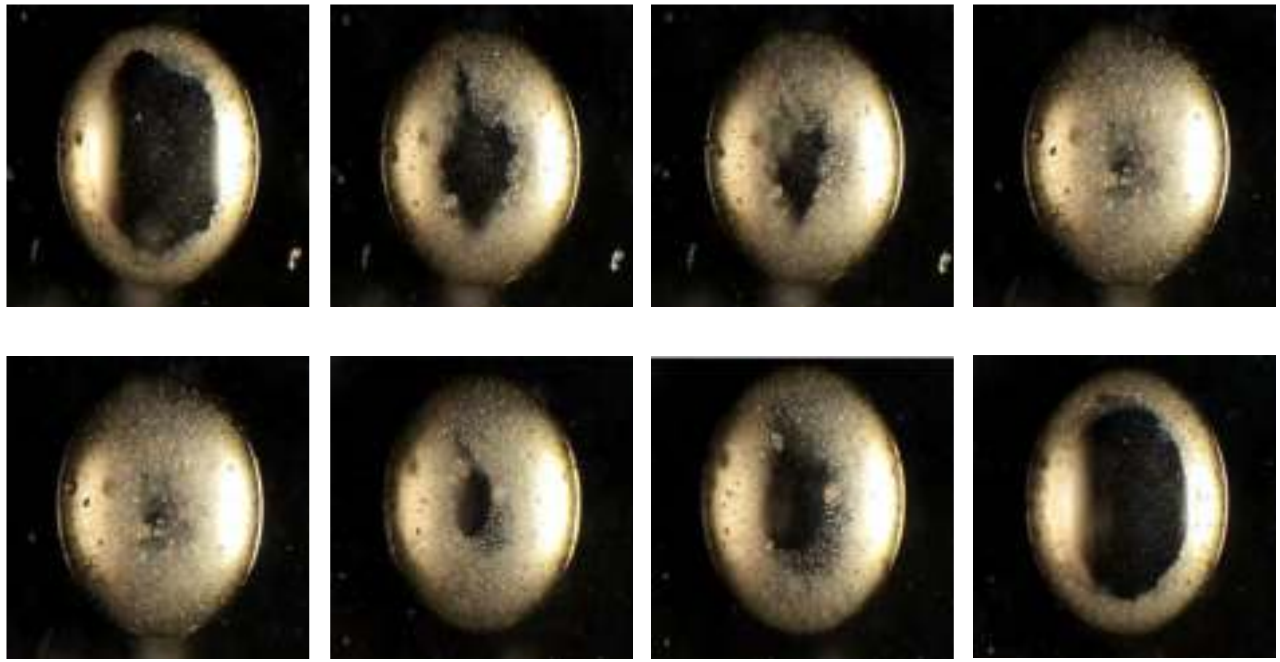
Chain formation inside a drop?

Electrorheological droplets for microfluidics
Electrorheological emulsions

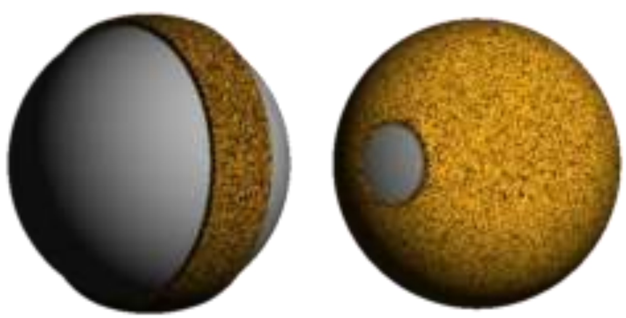
Is it possible to make electrorheological drops?

200 → 500 V/mm

200 ← 500 V/mm



Electro-hydrodynamic flow



Dipole-dipole interactions

Active pupil-like colloidal shell (opening - closing)

nature COMMUNICATIONS
Published 28 Jun 2013

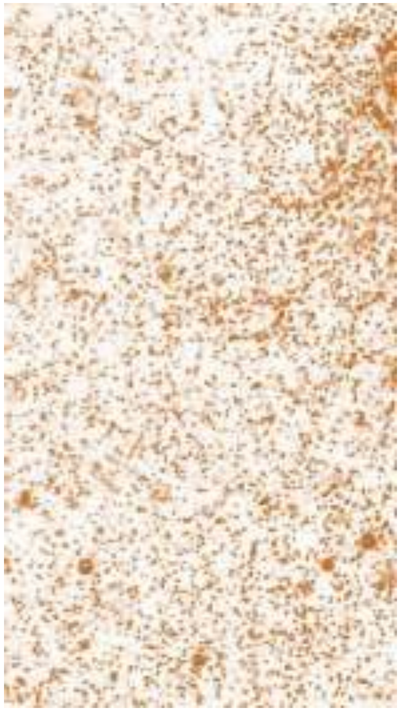
Active structuring of colloidal armour on liquid drops

Paul Dommersnes[1,2,3,4,*], Zbigniew Rozynek[1,*], Alexander Mikkelsen[1], Rene Castberg[2], Knut Kjerstad[1], Kjetil Hersvik[1] & Jon Otto Fossum[1,4,*]

NATURE COMMUNICATIONS | 4:2066 | DOI: 10.1038/ncomms3066

Active pupil-like colloidal shell (opening - closing)

Oil + particles in E-fields



PE beads

$\varepsilon_{oil} \sim \varepsilon_{particles}$

$\sigma_{oil} \sim \sigma_{particles}$

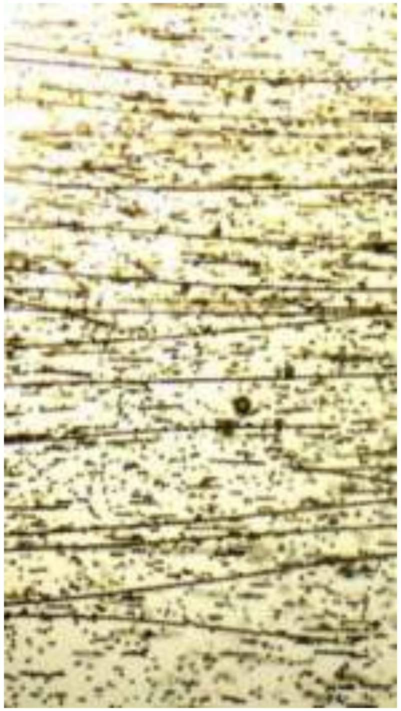
Very high E-field

Clay particles

$\varepsilon_{oil} < \varepsilon_{particles}$

$\sigma_{oil} < \sigma_{particles}$

Hundreds V/mm



Ag coated beads

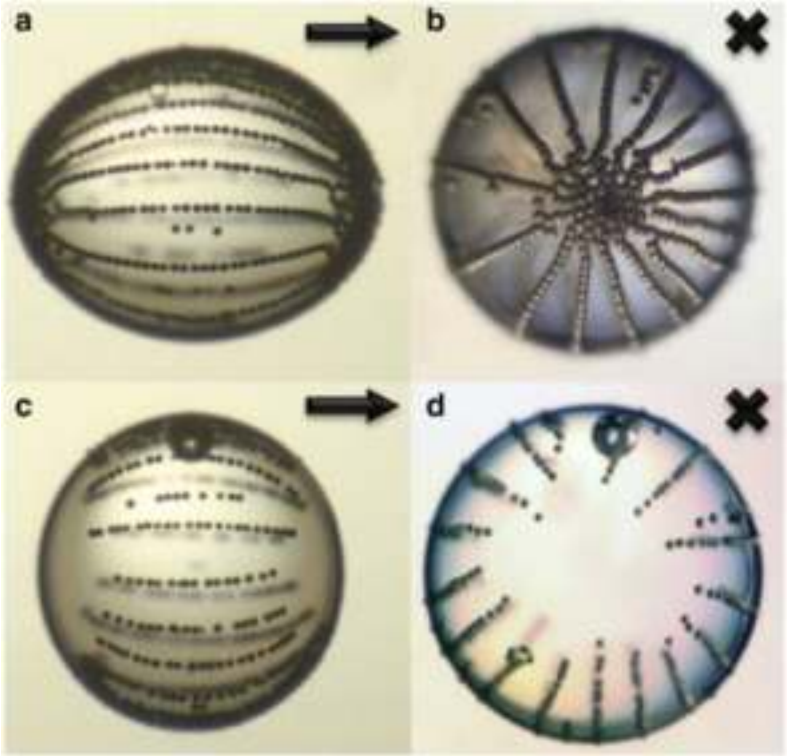
$\varepsilon_{oil} \ll \varepsilon_{particles}$

$\sigma_{oil} \ll \sigma_{particles}$

Tens V/mm

Particle dipole-dipole interactions

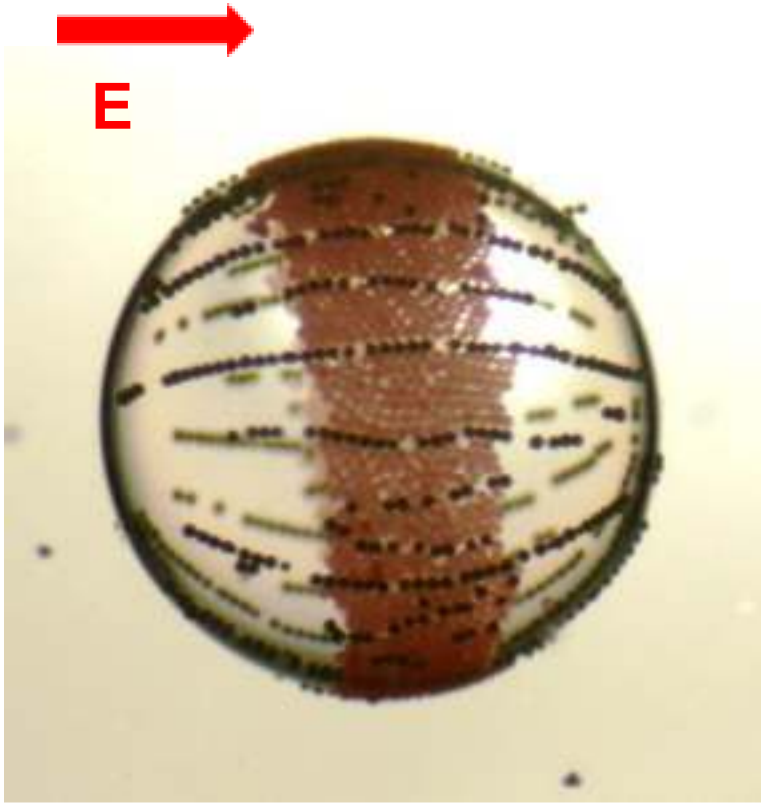
Drop “behind bars”



Matallic conducting beads on the surface of a silicone drop with a radius of about 1 mm embedded in castor oil

NOT POSSIBLE TO OBTAIN the Pupil-like effect

using either non-conductive PE beads or silver coated glass beads



E= 250 V/mm

No pupil-like colloidal shell for insulating or high conductive particles

Cite this: *Soft Matter*, 2011, **7**, 2600

www.rsc.org/softmatter

PAPER

Semi-permeable vesicles composed of natural clay†

Anand Bala Subramaniam,*[a] Jiandi Wan,[b] Arvind Gopinath[c] and Howard A. Stone*[b]

Received 21st November 2010, Accepted 3rd January 2011

DOI: 10.1039/c0sm01354d

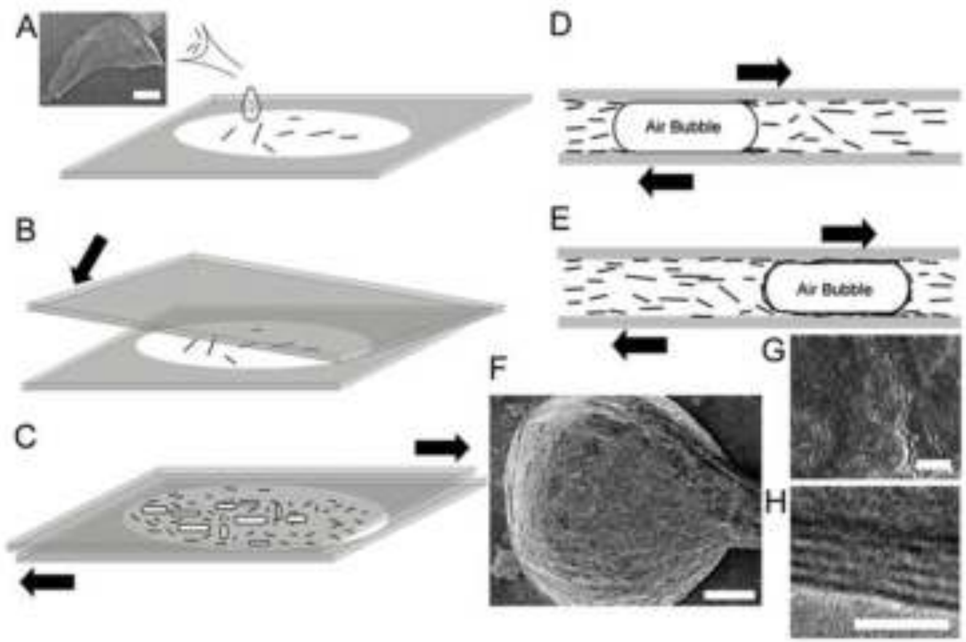


Fig. 1 Formation of clay armored bubbles. (A, inset) TEM image demonstrating the plate-like structure of the clay montmorillonite. (A) An aqueous suspension of clay is placed on a glass slide. (B) A second glass slide is engaged on the first glass slide, trapping pockets of gas in the process. (C) The slides are pressed together manually and sheared relative to each other. Conceptualization: (D) The air bubble is deformed in the narrow gap, the clay nanoplates align in the direction of shear and some are trapped at the wedges between the air–water interface and the glass slide. (E) Eventually the bubble picks up enough particles to be fully armored. (F) SEM images of a dried clay armored bubble. (G) Higher magnification view of the clay layer, which appears smooth and continuous with no pores. (H) HRTEM image of the clay armored bubble wall showing the multilayer structure. Scale bars: (A, inset) 100 nm, (F) 20 μm, (G) 200 nm and (H) 10 nm.

"Sorry. I thought a joke would break the tension."

Case 1: Partly covered drops ⇒ Coalescence
Case 2: Fully covered drops ⇒ No coalesence

Fully covered drops do not coalesce ⇒ Pickering emulsions: Experiments at NTNU Trondheim

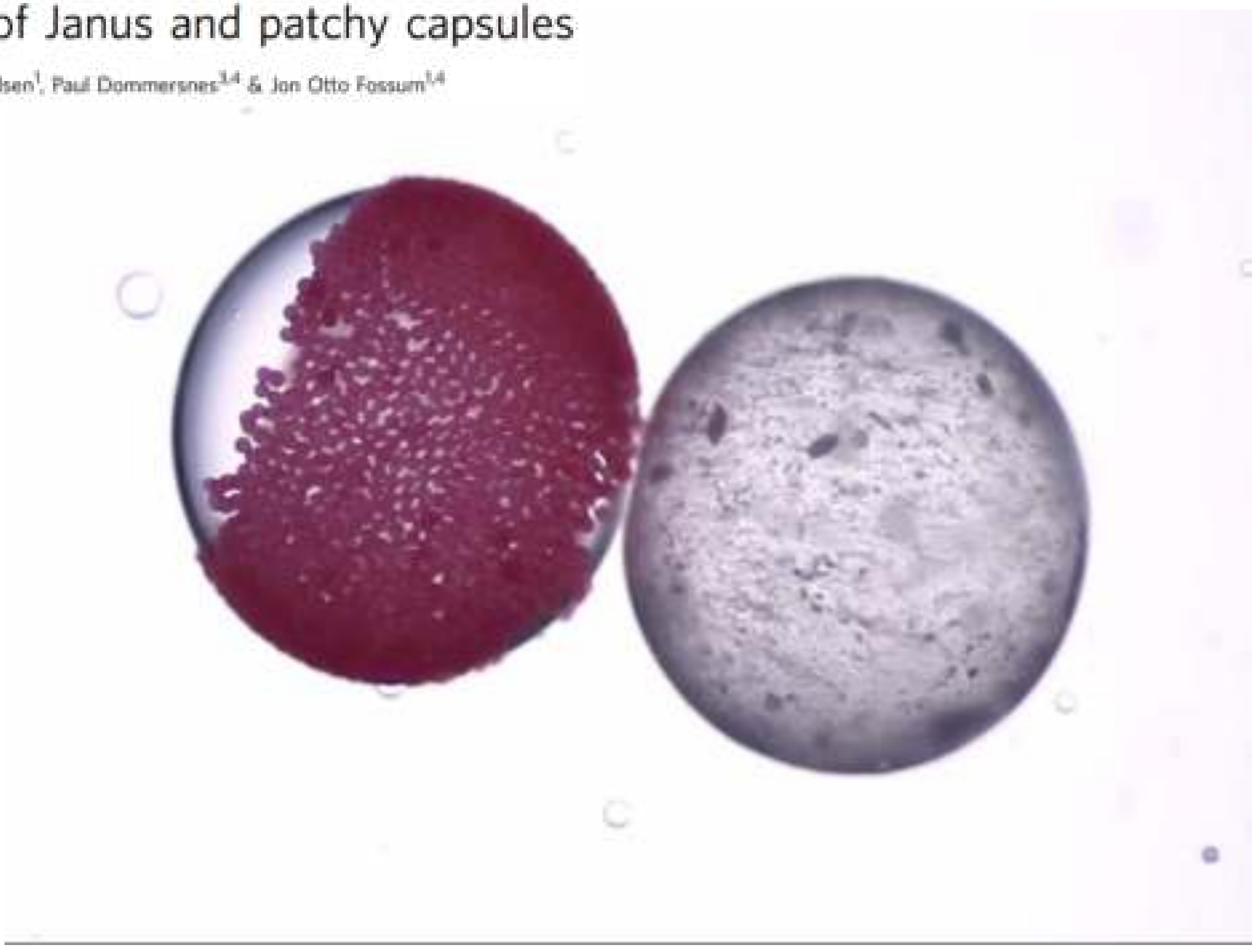
nature COMMUNICATIONS

ARTICLE

Received 20 Nov 2013 | Accepted 24 Apr 2014 | Published 23 May 2014 OPEN

Electroformation of Janus and patchy capsules

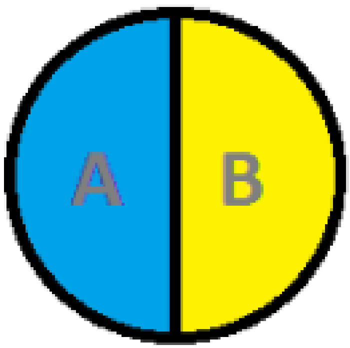
Zbigniew Rozynek[1,2], Alexander Mikkelsen[1], Paul Dommersnes[3,4] & Jon Otto Fossum[1,4]



Janus shells with clay and PE particles, Experiments at NTNU Trondheim

In ancient Roman religion and myth, Janus is the god of beginnings and transitions, thence also of gates, doors, passages, endings and time.

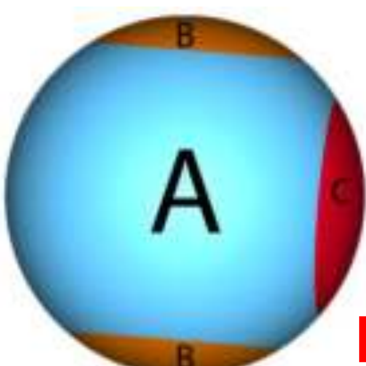
Usually depicted with **two faces**, looking to the future and to the past



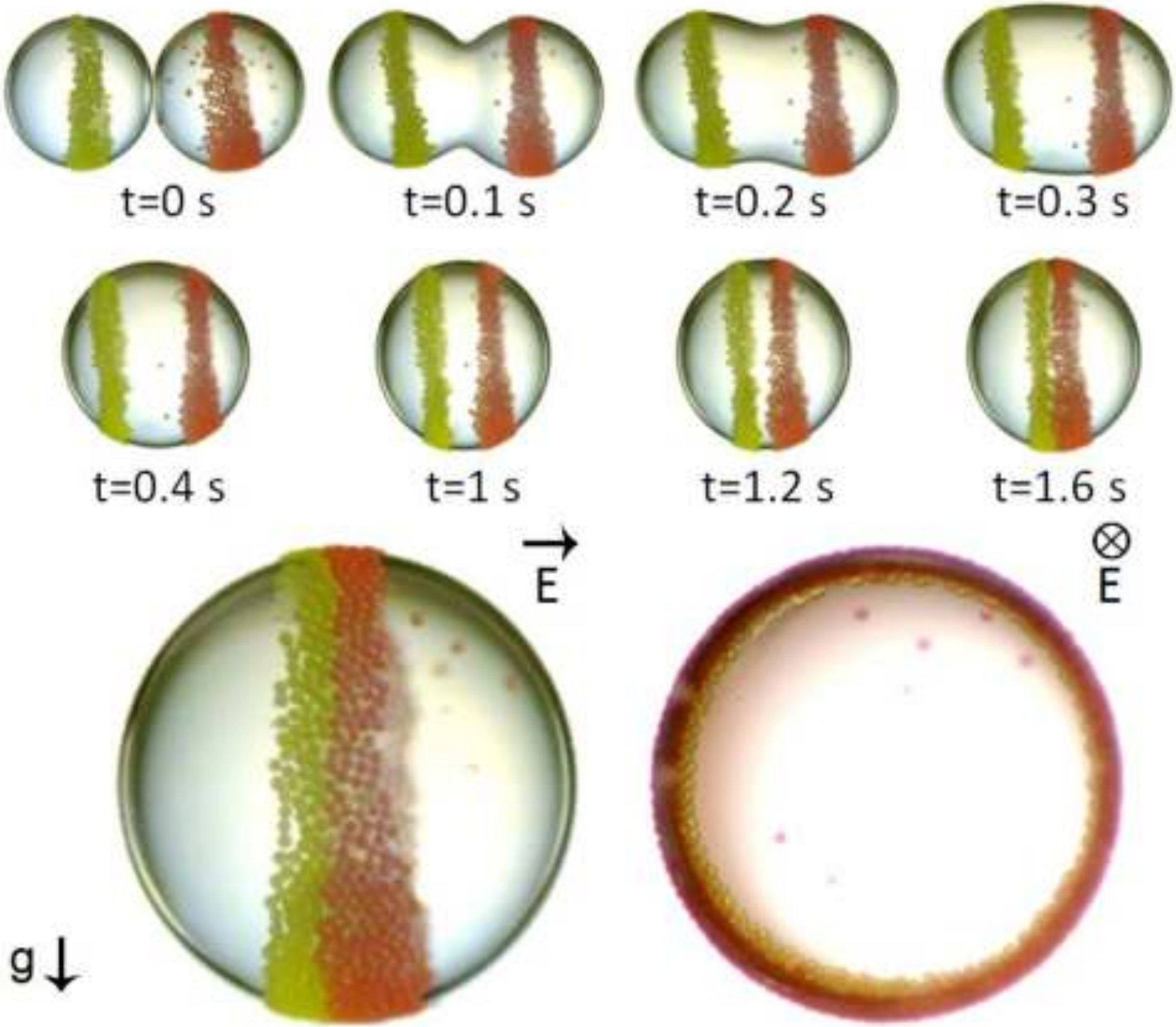
Pierre-Gilles de Gennes Nobel Prize lecture, 1991

Janus particles or capsules

The god Janus had two faces. The grains have two sides: one apolar, and the other polar. Thus, they have certain features in common with surfactants. But there is an interesting difference if we consider the films which they make, for instance at a water - air interface. A dense film of a conventional surfactant is quite impermeable. On the other hand, a dense film of Janus grains always has some interstices between the grains, and allows for chemical exchange between the two sides; "the skin can breathe".



Patchy particles or capsules



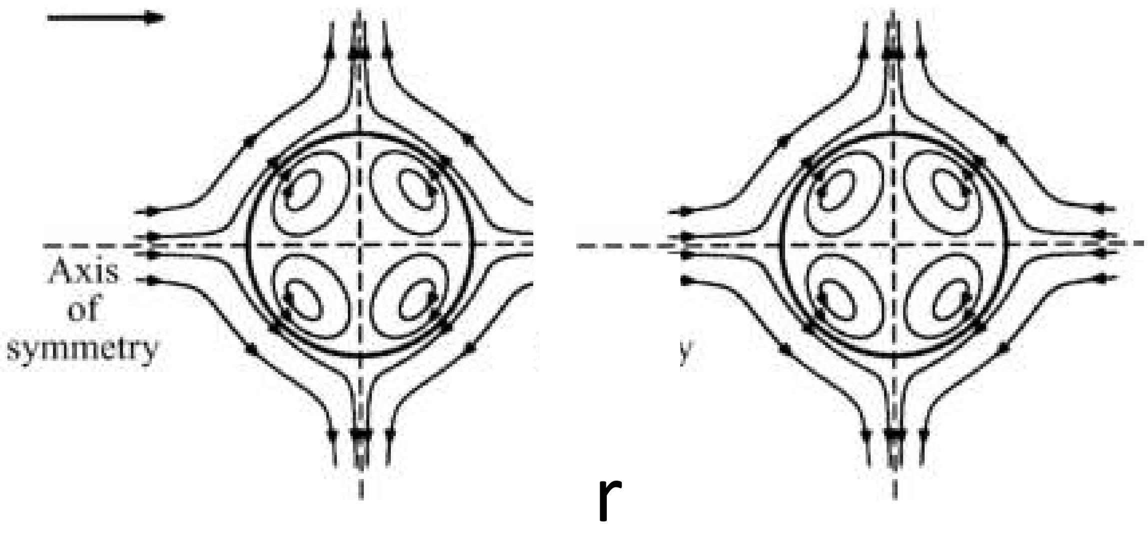
Final state viewed perpendicular and parallel to the E-Field

Fabrication of Janus ribbon: Experiments at NTNU Trondheim

J. Fluid Mech. (1998), vol. 368, pp. 359–375. Printed in the United Kingdom 359

Electrohydrodynamic deformation and interaction of drop pairs

By J. C. BAYGENTS[1], N. J. RIVETTE[1] AND H. A. STONE[2]



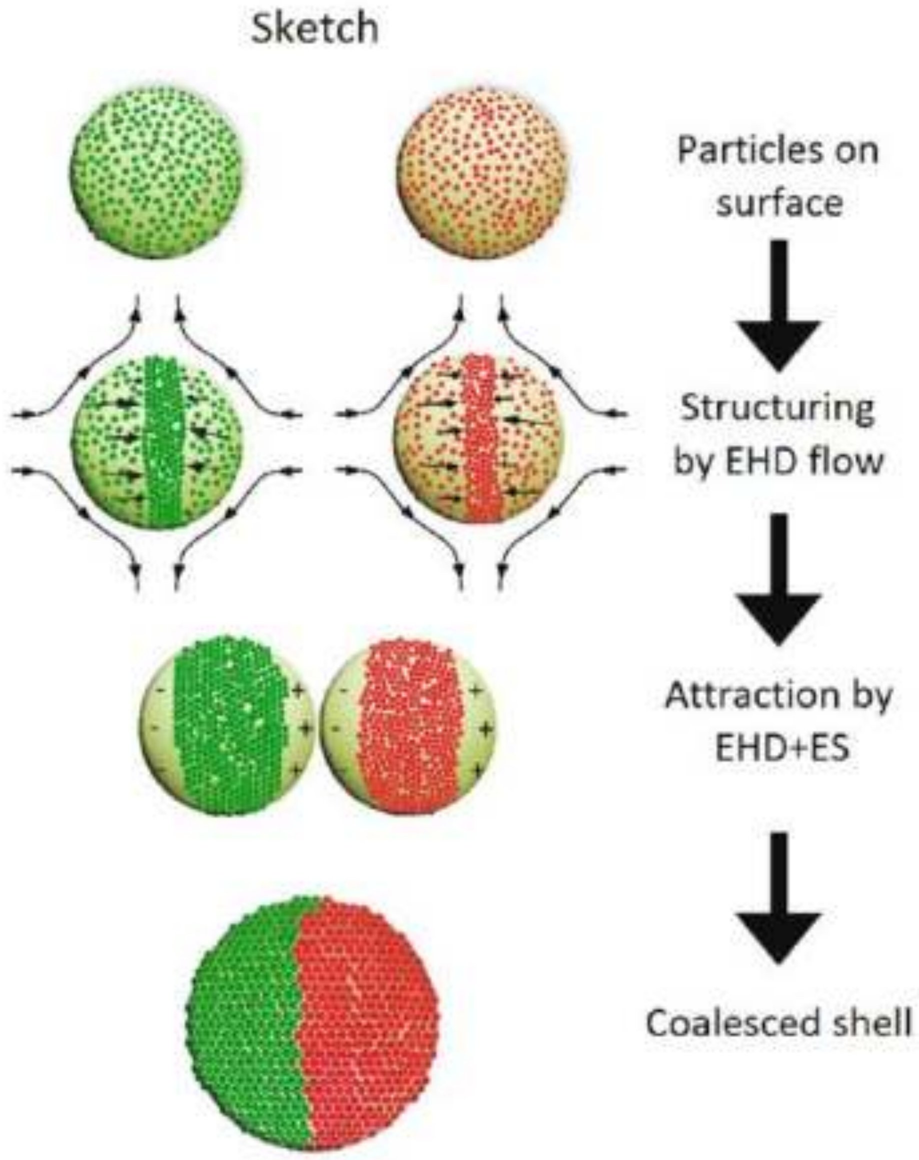
$$V_{hydro} \propto \frac{1}{r}$$

$$V_{dipole} \propto \frac{1}{r^3}$$

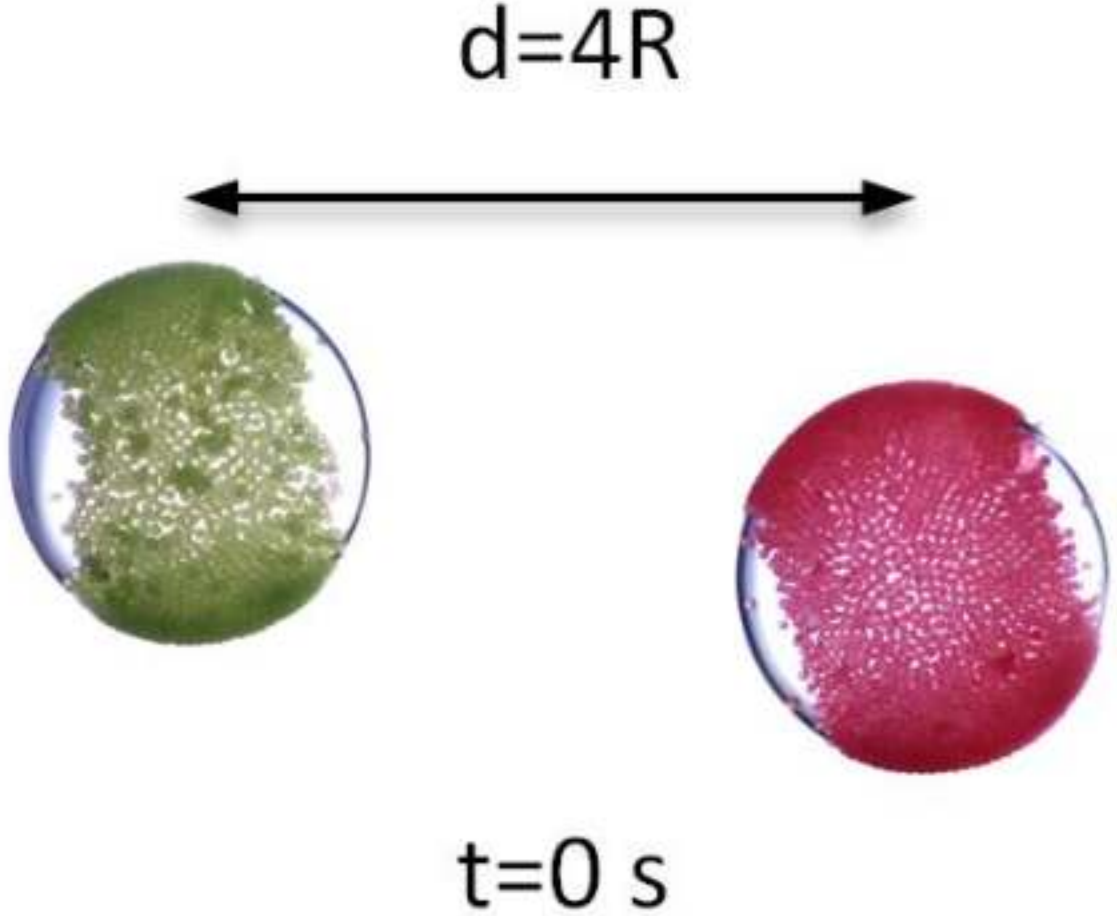
$\hat{\tau} > \tau$ Attractive hydrodynamic interaction

$\hat{\tau} < \tau$ Repulsive hydrodynamic interaction

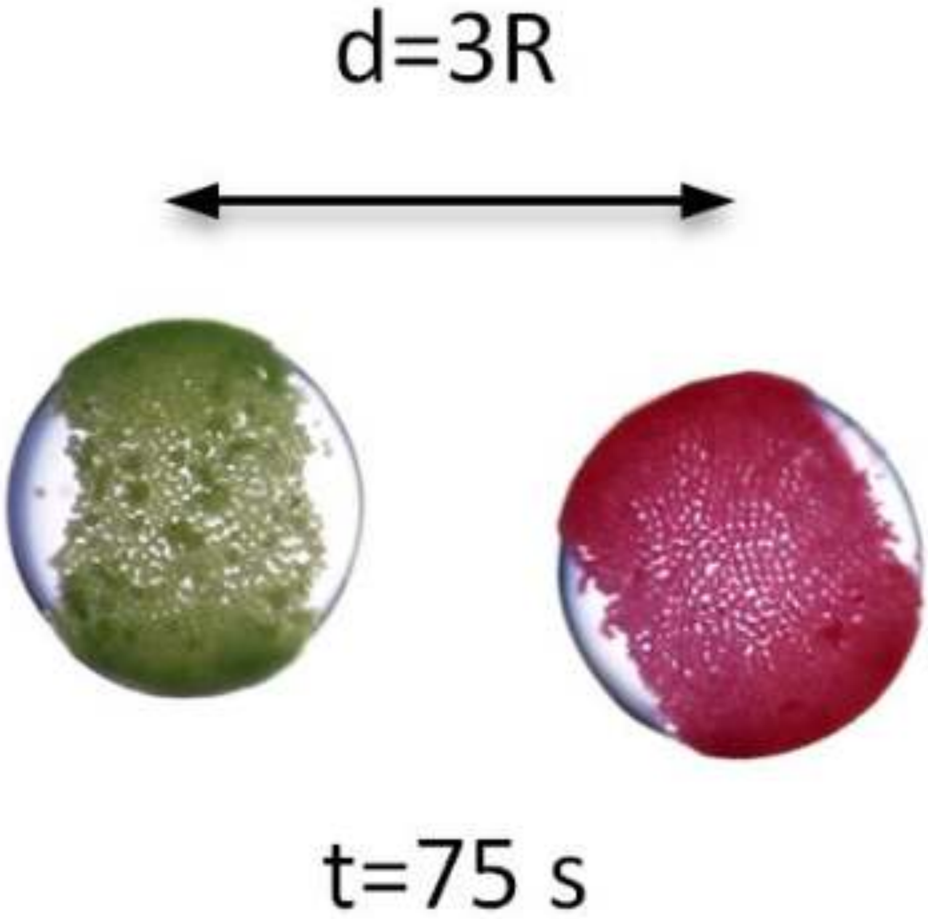
Hydrodynamic interactions are stronger than dipole-dipole interactions



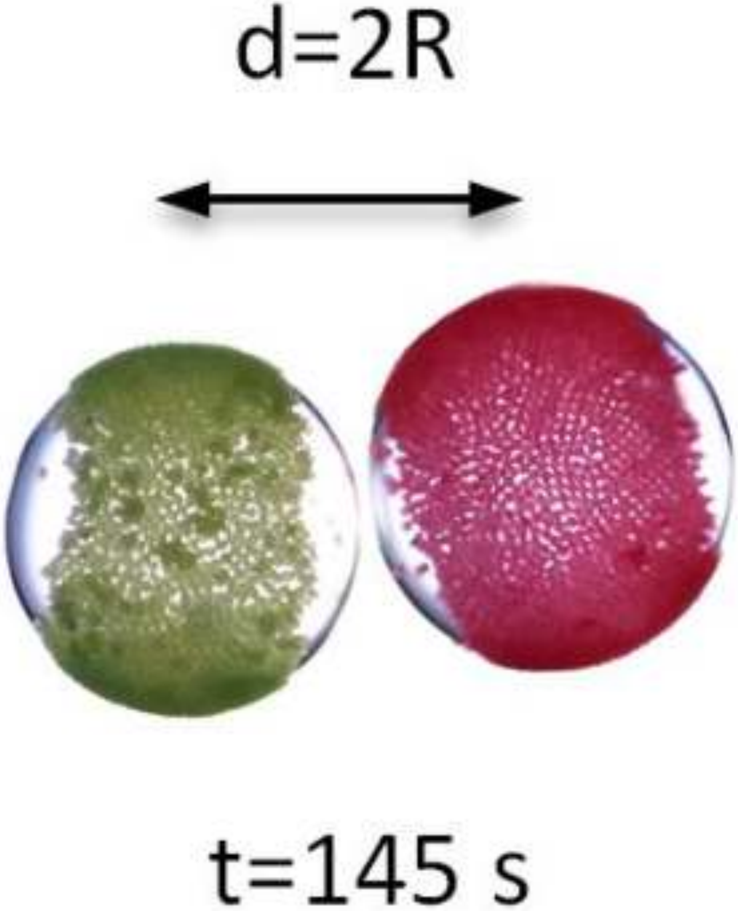
Fabrication of Janus shell: Experiments at NTNU Trondheim

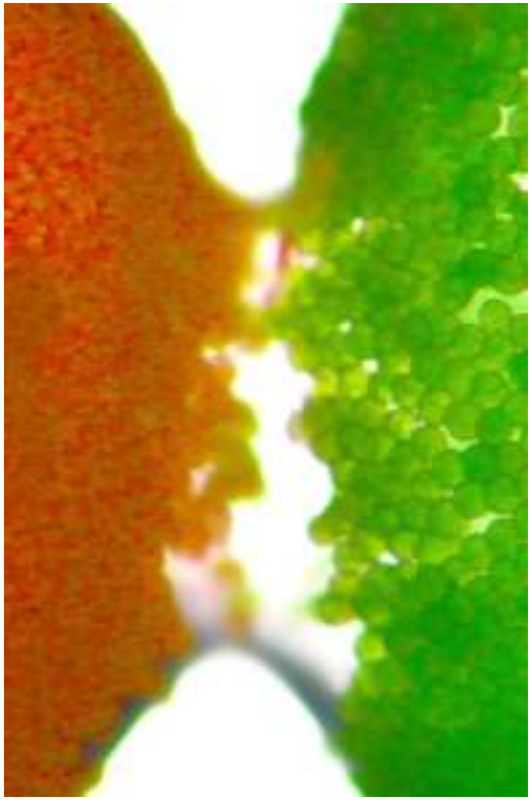


Fabrication of Janus shell: Experiments at NTNU Trondheim

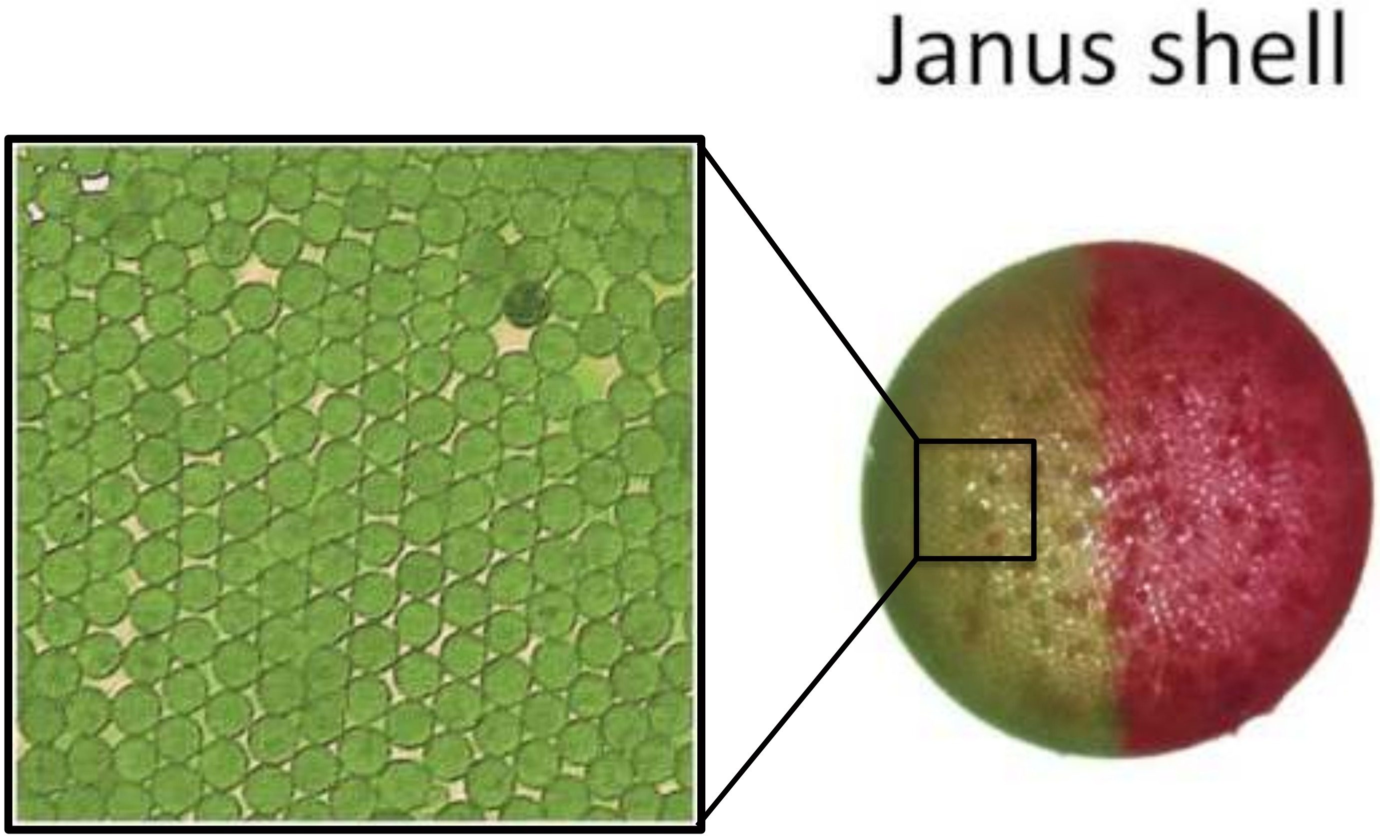


Fabrication of Janus shell: Experiments at NTNU Trondheim

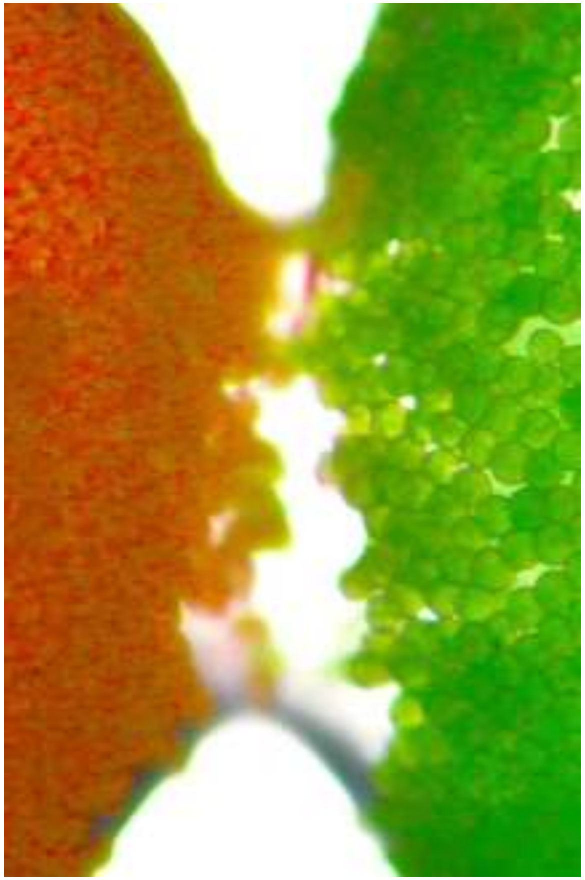




Fabrication of Janus shell: Experiments at NTNU Trondheim



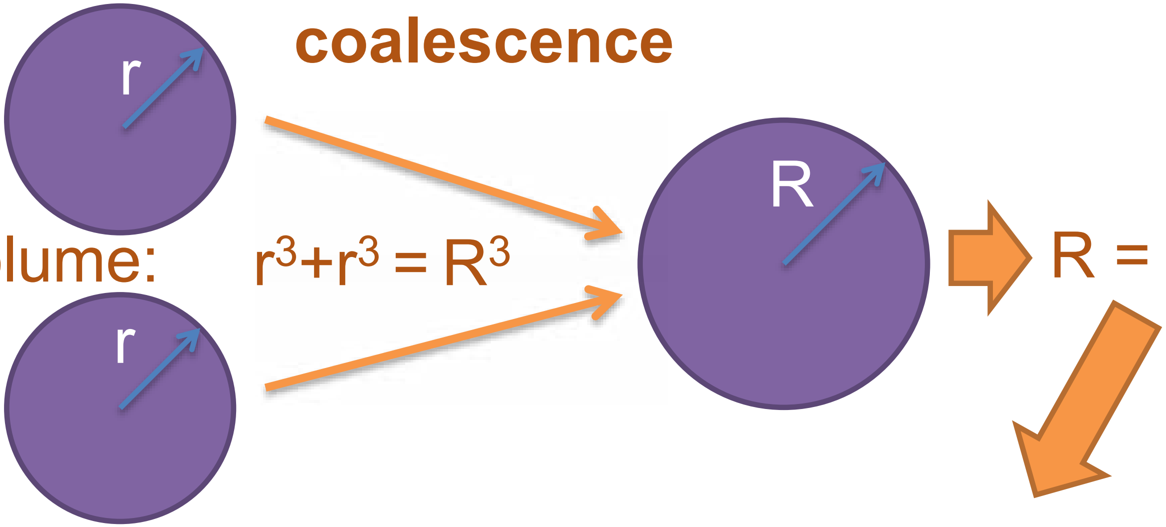
Hexagonal packing: Experiments at NTNU Trondheim



The ribbon formations bring the particles **«away from»** the «electric polar areas» of the drops, i.e. enabling coalescence.

Activated coalescence

Reduction of surface area by coalescence:



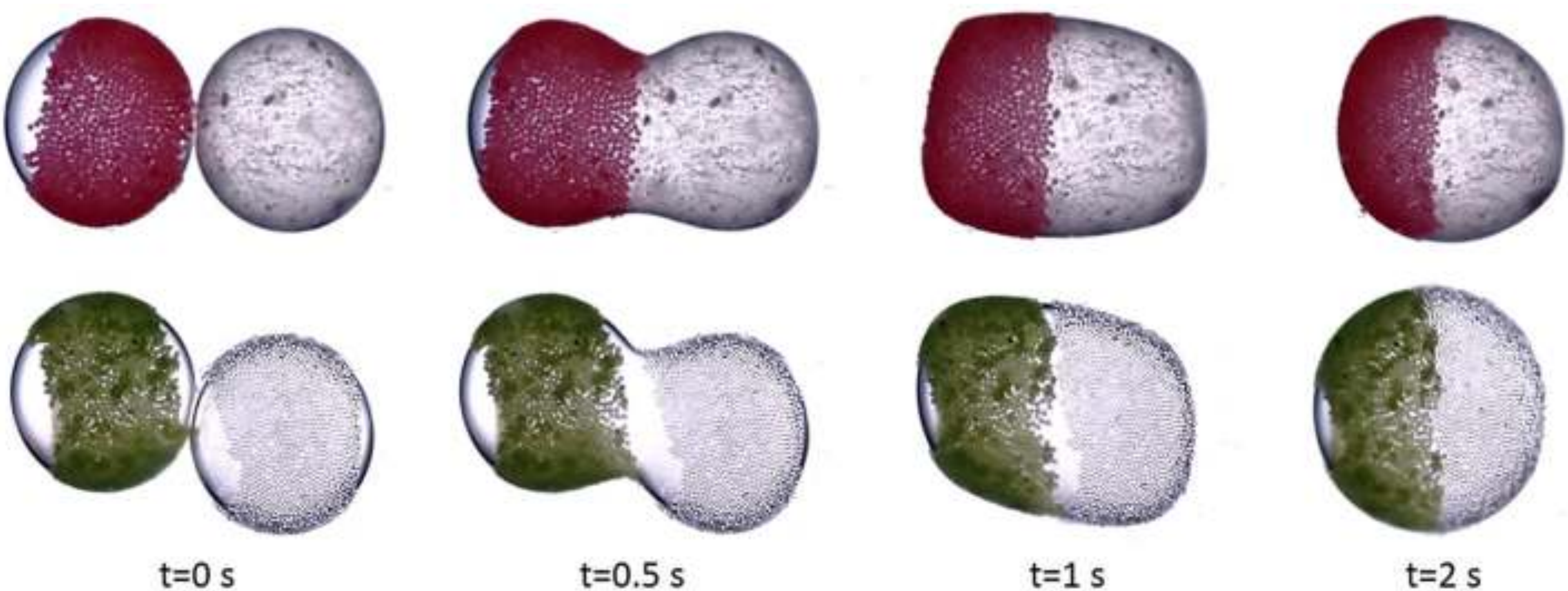
Volume: $r^3 + r^3 = R^3$

$R = 2^{1/3} r \approx 1.25\, r$

Area: $R^2 = 2^{-1/3} 2r^2 = 2^{-1/3}(r^2 + r^2\ )$

$A_{new} \approx 0.8\, A_{initial}$

⇒ Final drop can be fully covered even if the original drops are not



Janus shells with clay, PE or PS particles:
Experiments at NTNU Trondheim

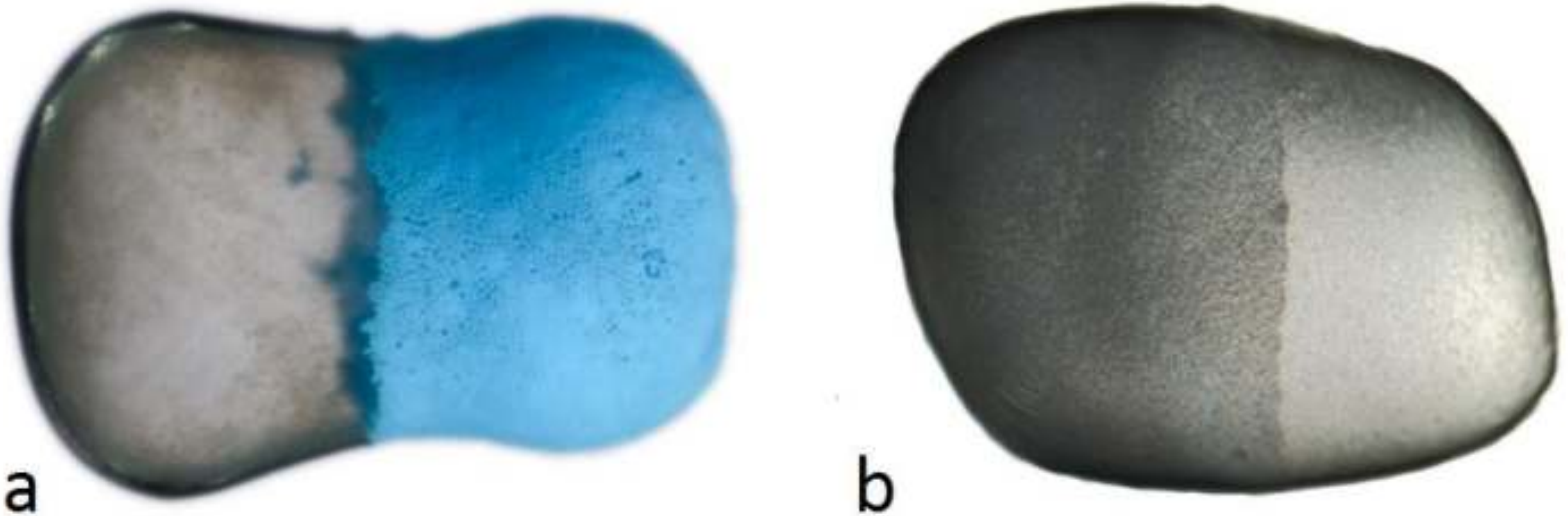
Janus shells with clay and PE particles:
Experiments at NTNU Trondheim

Spherical Janus shell: 1 μm and 500 nm particles:
Experiments at NTNU Trondheim

Arrested shells – symmetric:
Experiments at NTNU Trondheim

Arrested shells – asymmetric:
Experiments at NTNU Trondheim

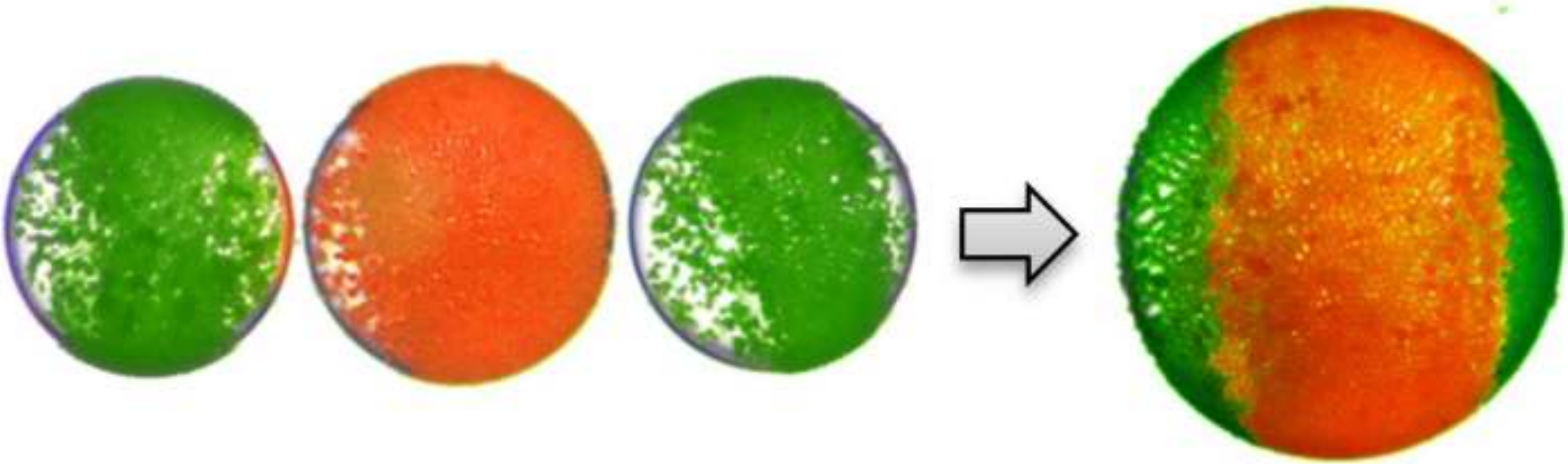
Arrested shells – asymmetric:
Experiments at NTNU Trondheim



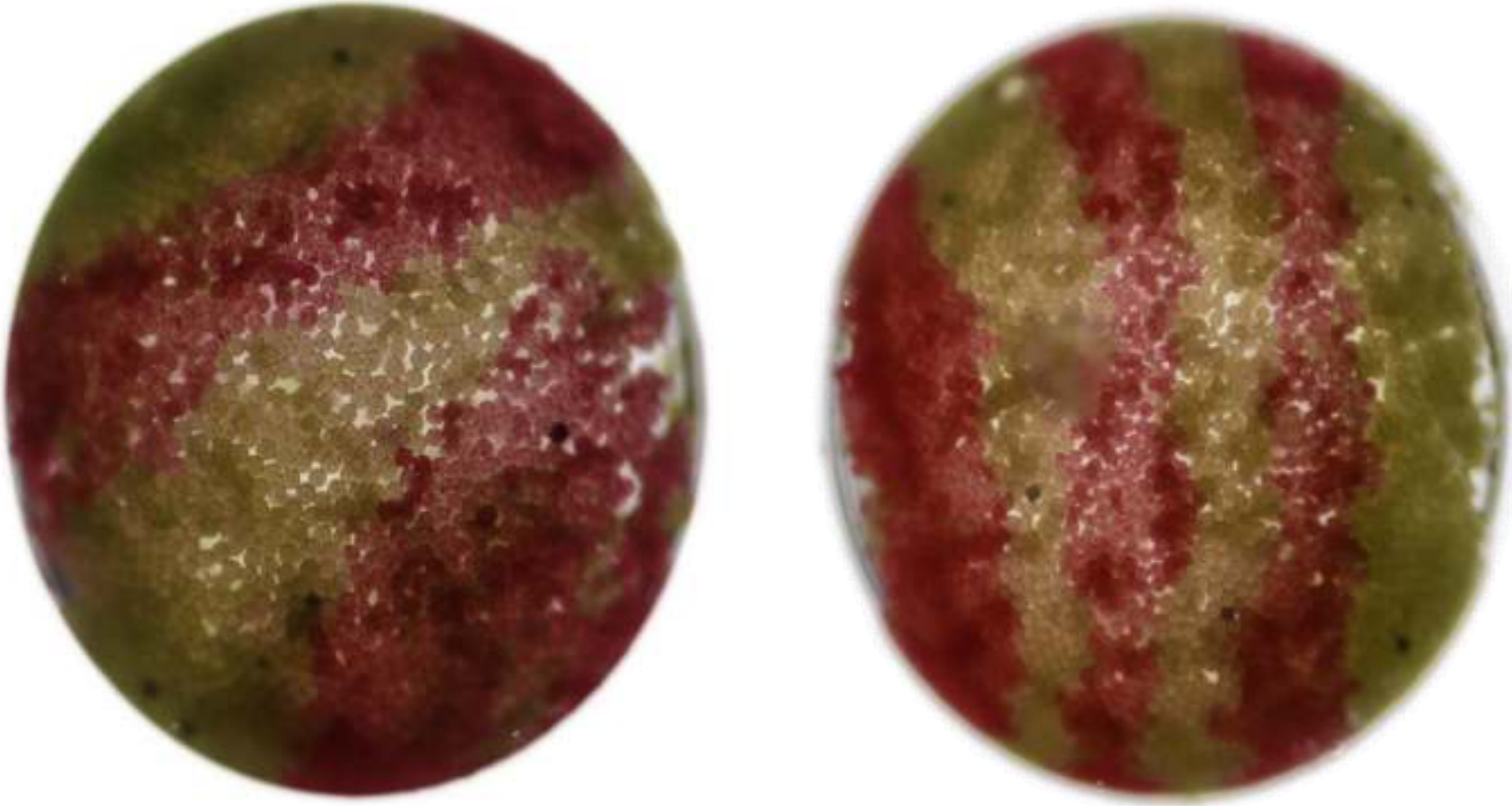
glass (500 nm) and blue PE (20 μm) particles

PS (1 μm) and clay mineral (~1 μm) particles

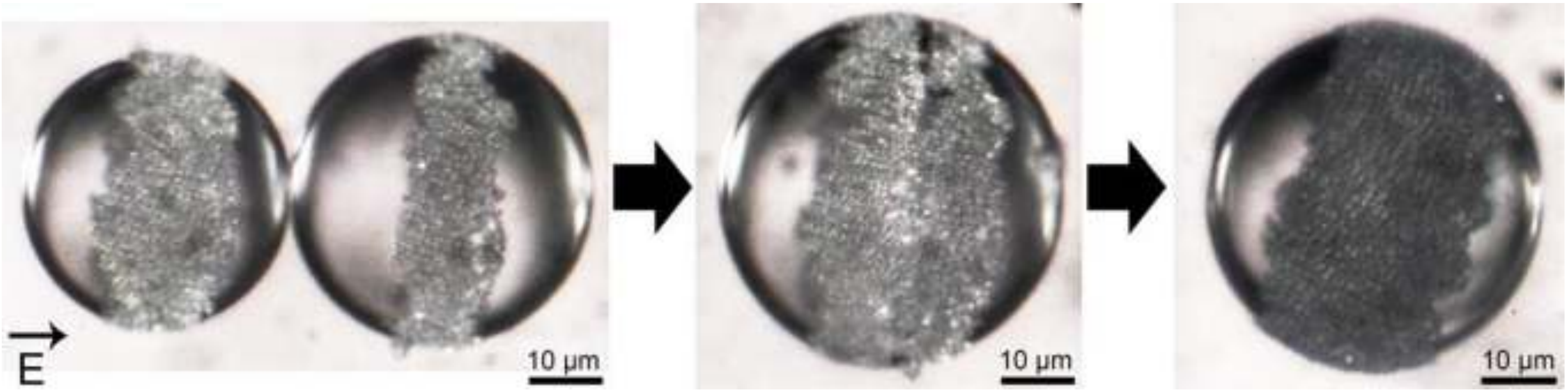
Arrested shells : Small particles: Experiments at NTNU Trondheim



Patchy shells: Experiments at NTNU Trondheim

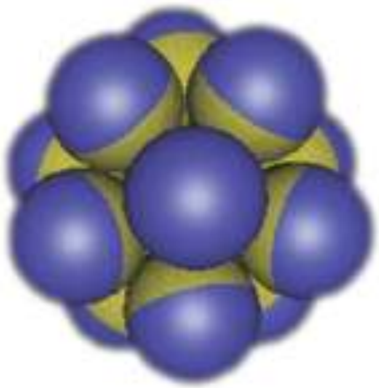


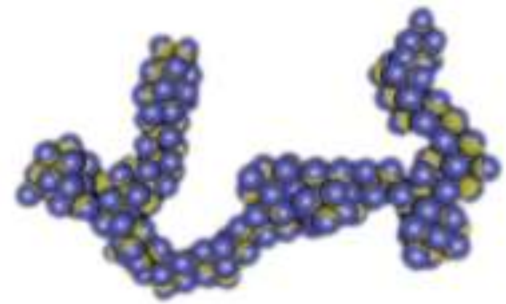
Patchy shells: Experiments at NTNU Trondheim



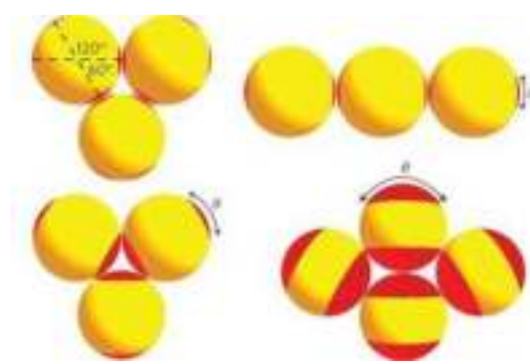
Smaller droplets?: Experiments at NTNU Trondheim

Janus shells

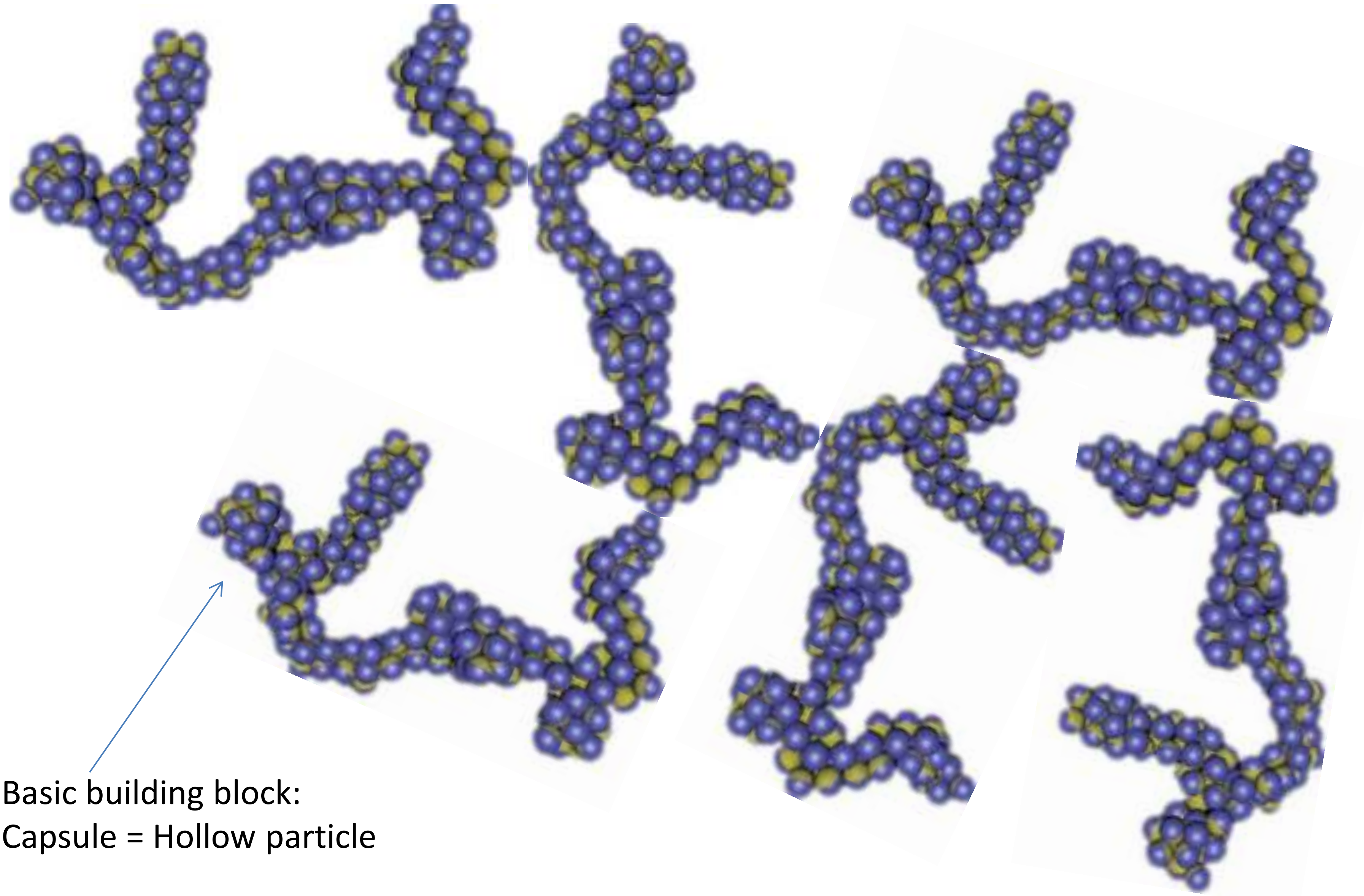




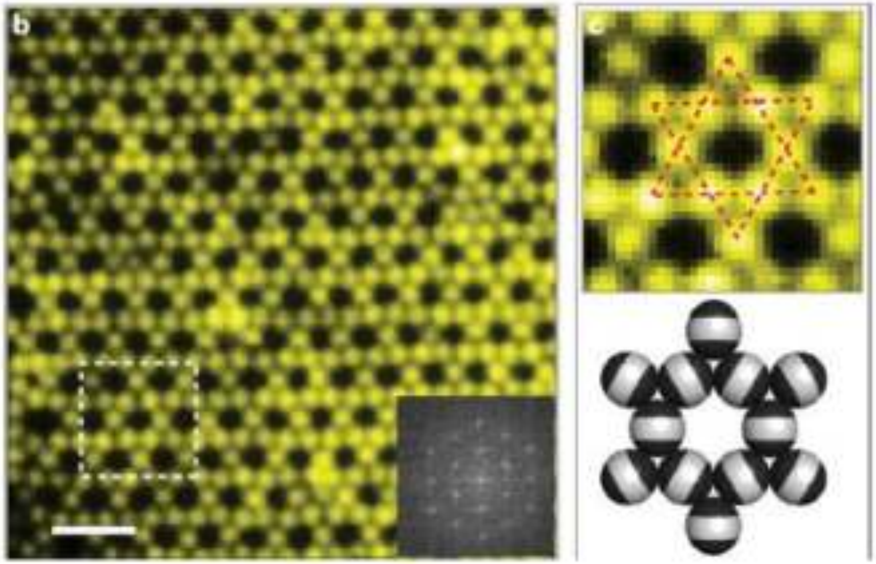
Patchy shells



Future fabrication of **hollow structures?**

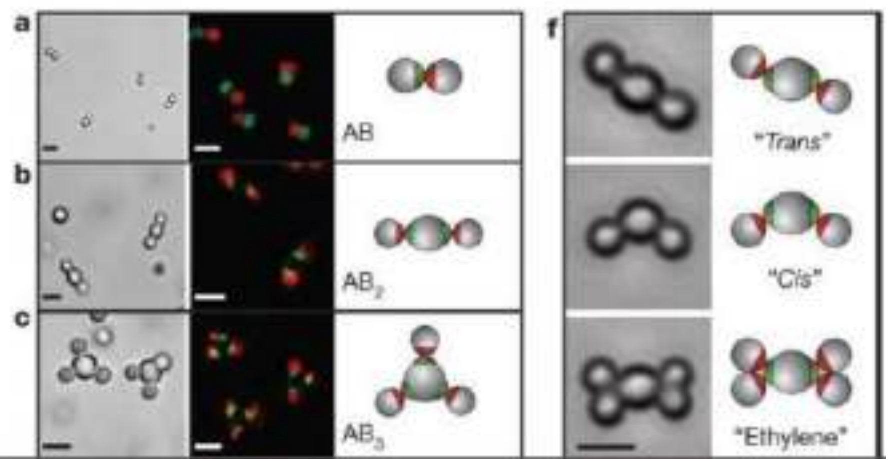


Example of complex hollow structure

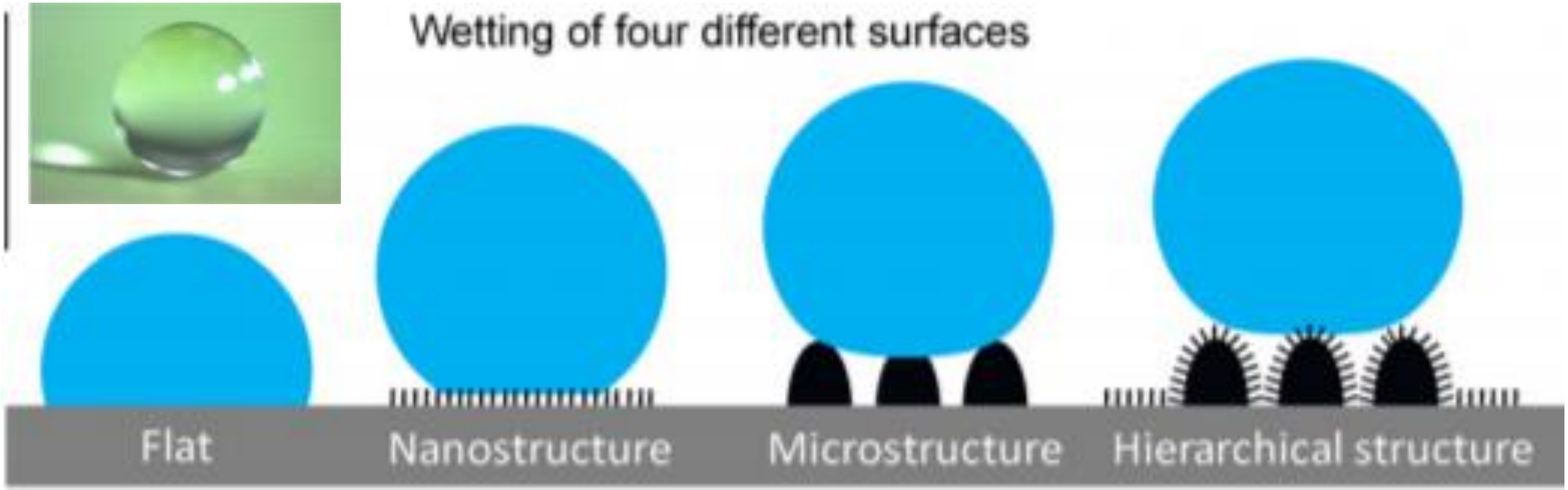


Patchy colloidal "molecules"
David Pine Group, Nature 2013

"Kagome lattice"
Q. Chen, S. C. Bae & S. Granick,
Nature 2012



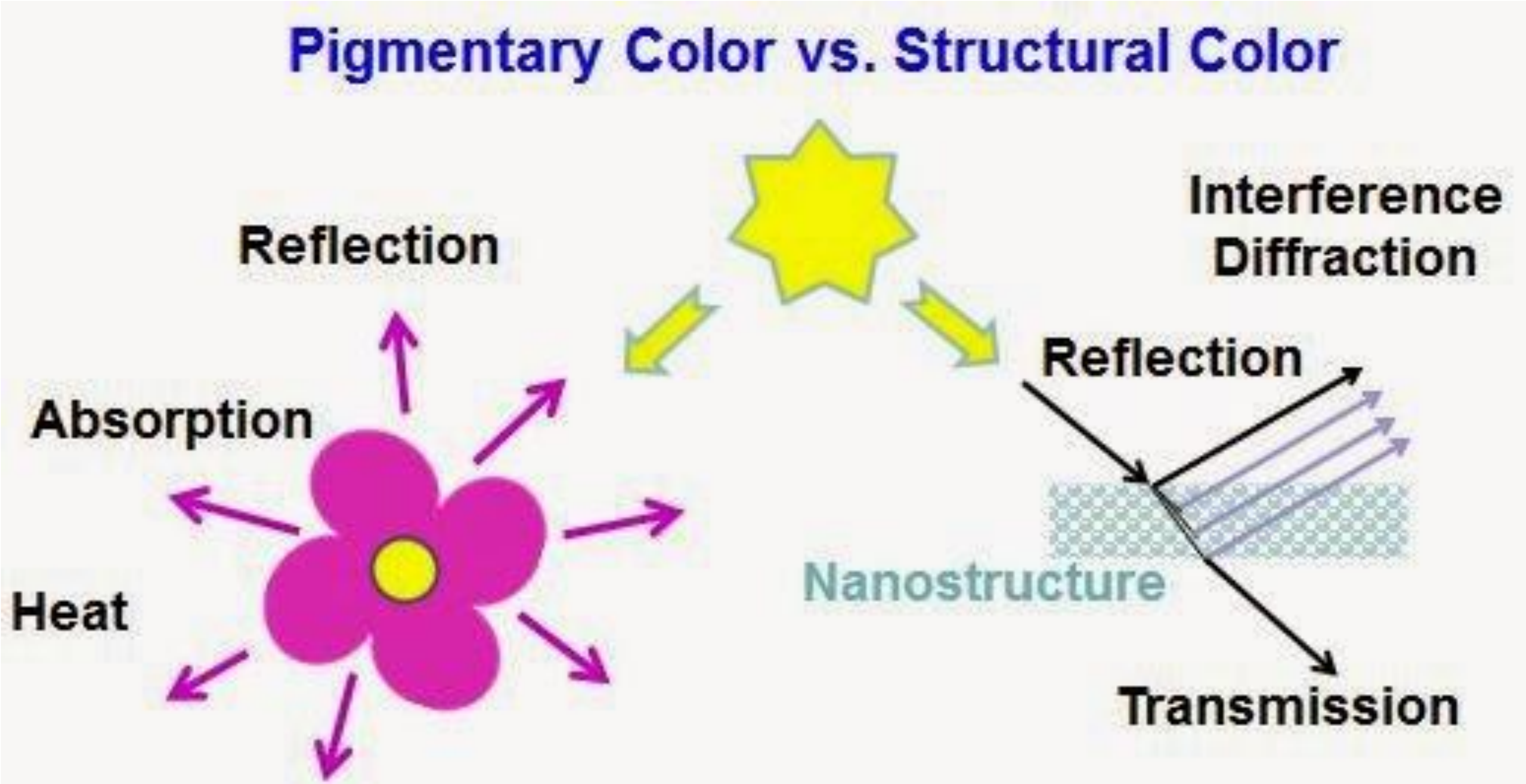
Self-assembly into (ordered) structures



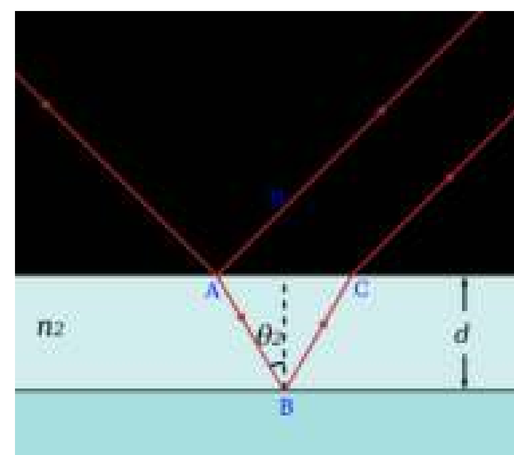
Schematics of wetting of four different surfaces. The largest contact area between the droplet and the surface is given in flat and micro-structured surfaces, is reduced in nano-structured surfaces, and is minimized in hierarchical (nano-micro) structured surfaces. This contains the principle of the so-called self-cleaning Lotus leaf effect, depicted to the left.

Natural and biomimetic artificial surfaces for super-hydrophobicity, self-cleaning, low adhesion, and drag reduction, B. Bhushan, Y. C. Jung, Progress in Materials Science 56, 1-108 (2011)

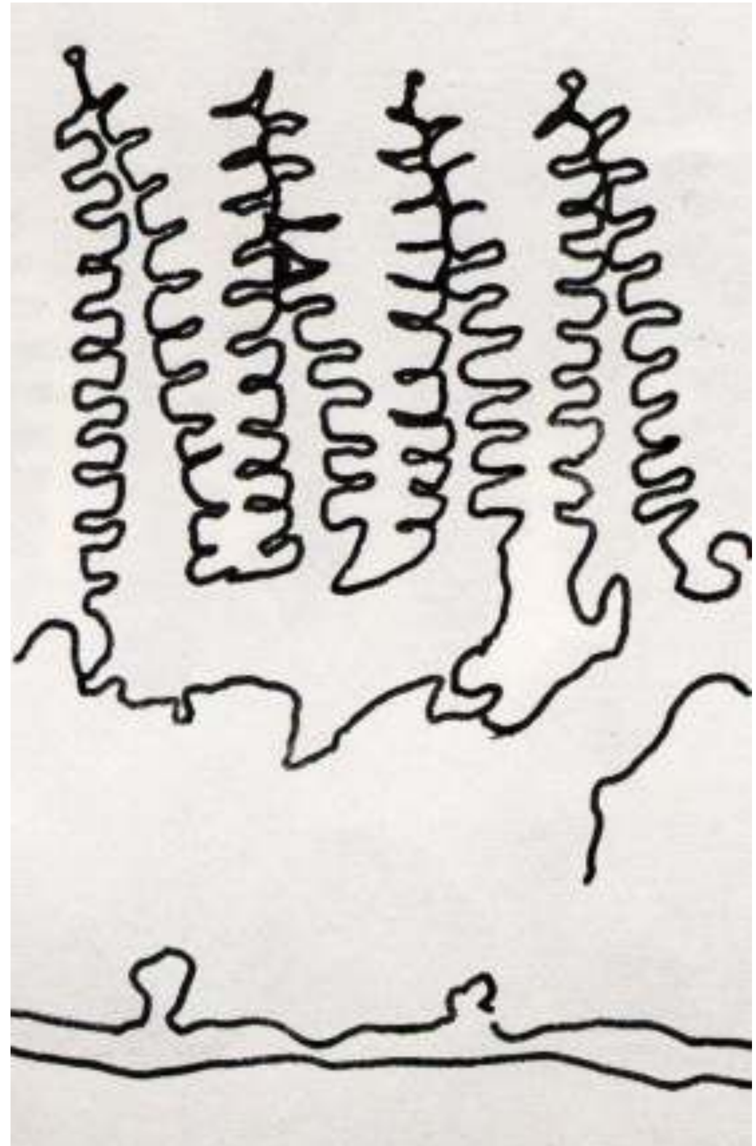
Peacock feathers: Brown pigment + nanostructures



When light falls on a thin film, the waves reflected from the upper and lower surfaces travel different distances depending on the angle, so they interfere.



Butterfly wing at different magnifications reveals mesostructured chitin acting as a diffraction grating



Article | OPEN

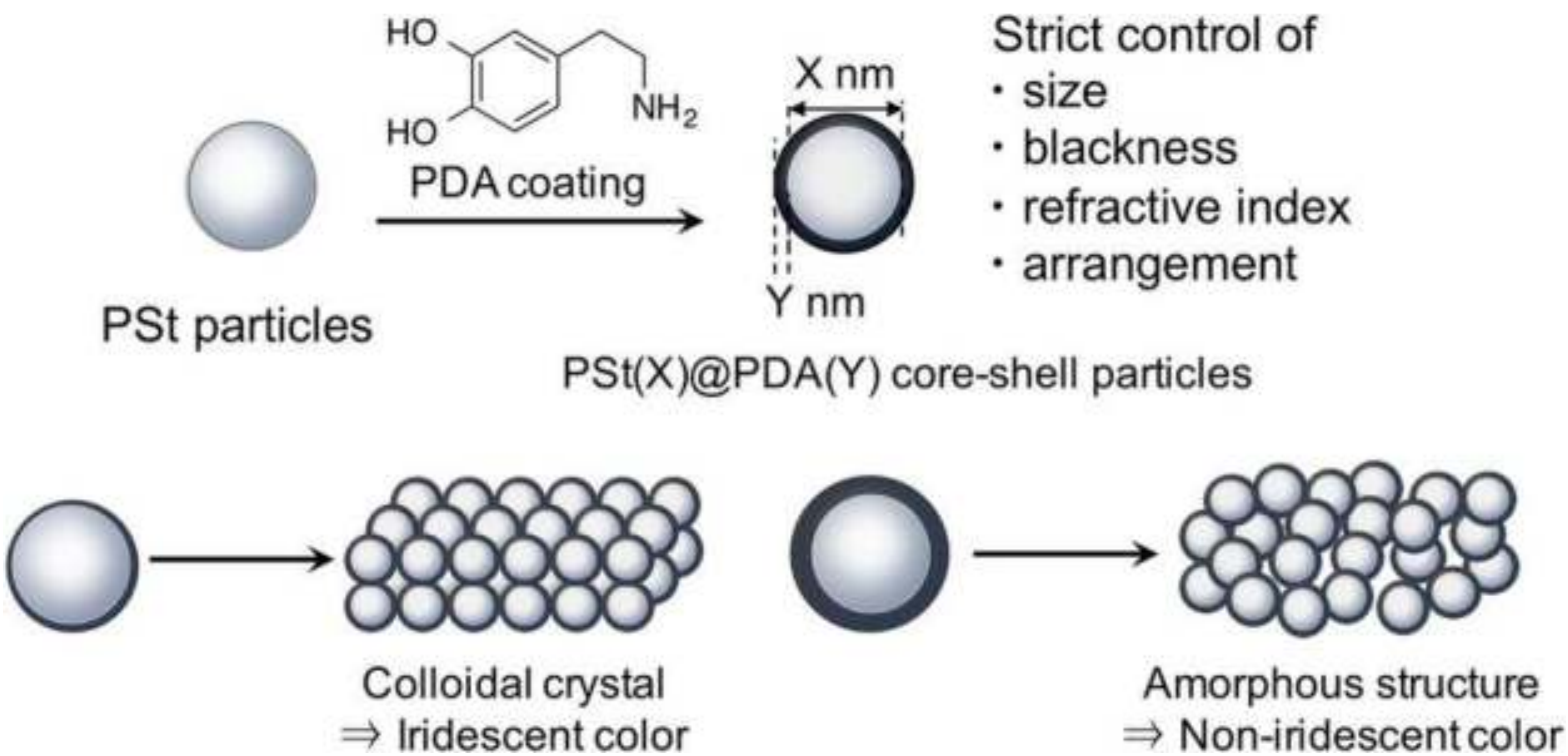
Full-Color Biomimetic Photonic Materials with Iridescent and Non-Iridescent Structural Colors

Ayako Kawamura, Michinari Kohri, Gen Morimoto, Yuri Nannichi, Tatsuo Taniguchi & Keiki Kishikawa

Scientific Reports **6**, Article number: 33984 (2016)
doi:10.1038/srep33984
Download Citation
Materials for optics
Optical materials

Received: 04 August 2016
Accepted: 06 September 2016
Published online: 23 September 2016

Polydopamine (PDA) shell layers
+ core polystyrene (PSt) particles



Article | OPEN

Photonic crystals cause active colour change in chameleons

Jérémie Teyssier, Suzanne V. Saenko, Dirk van der Marel & Michel C. Milinkovitch

Nature Communications 6, Article number: 6368 (2015)
doi:10.1038/ncomms7368
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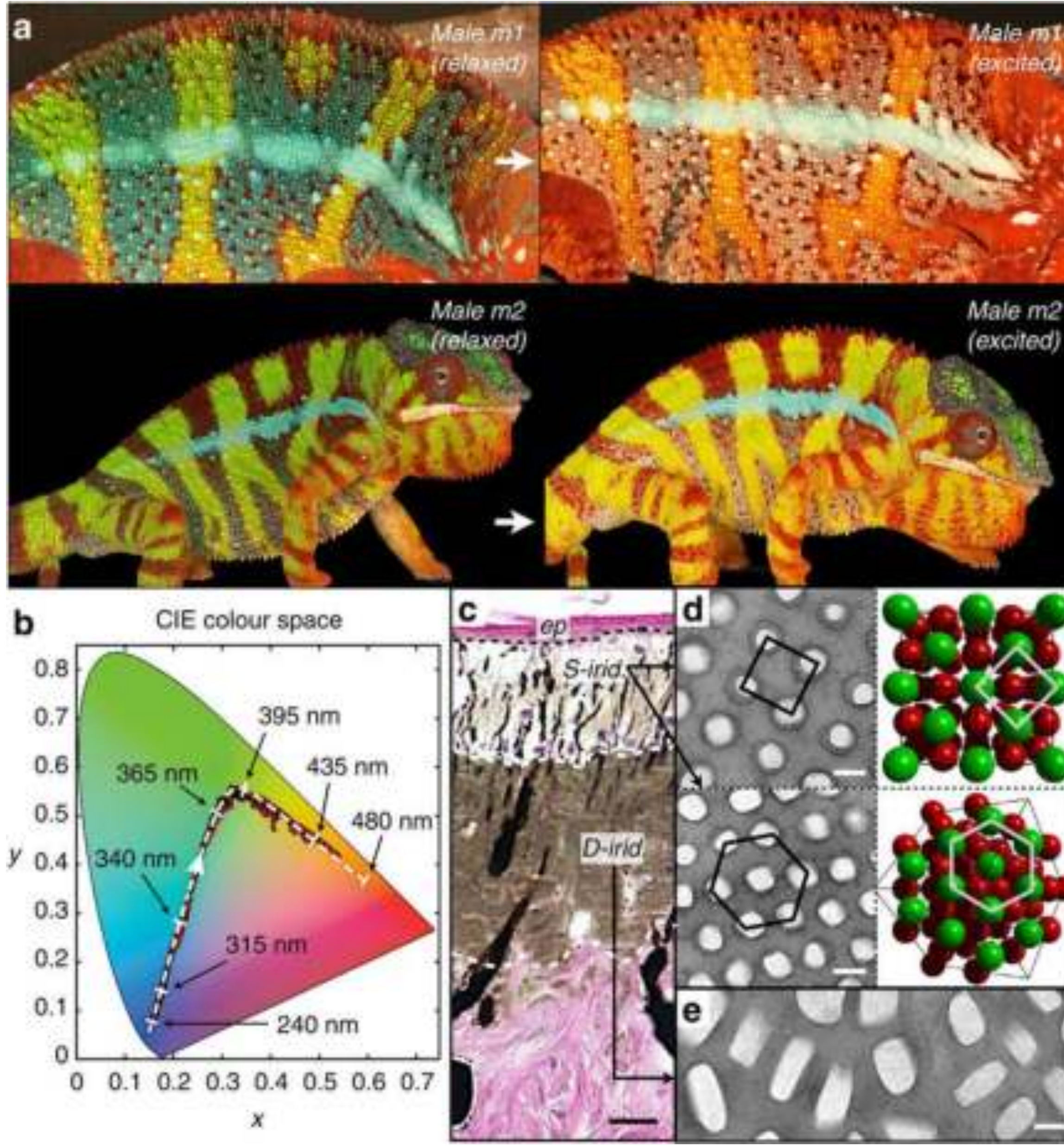
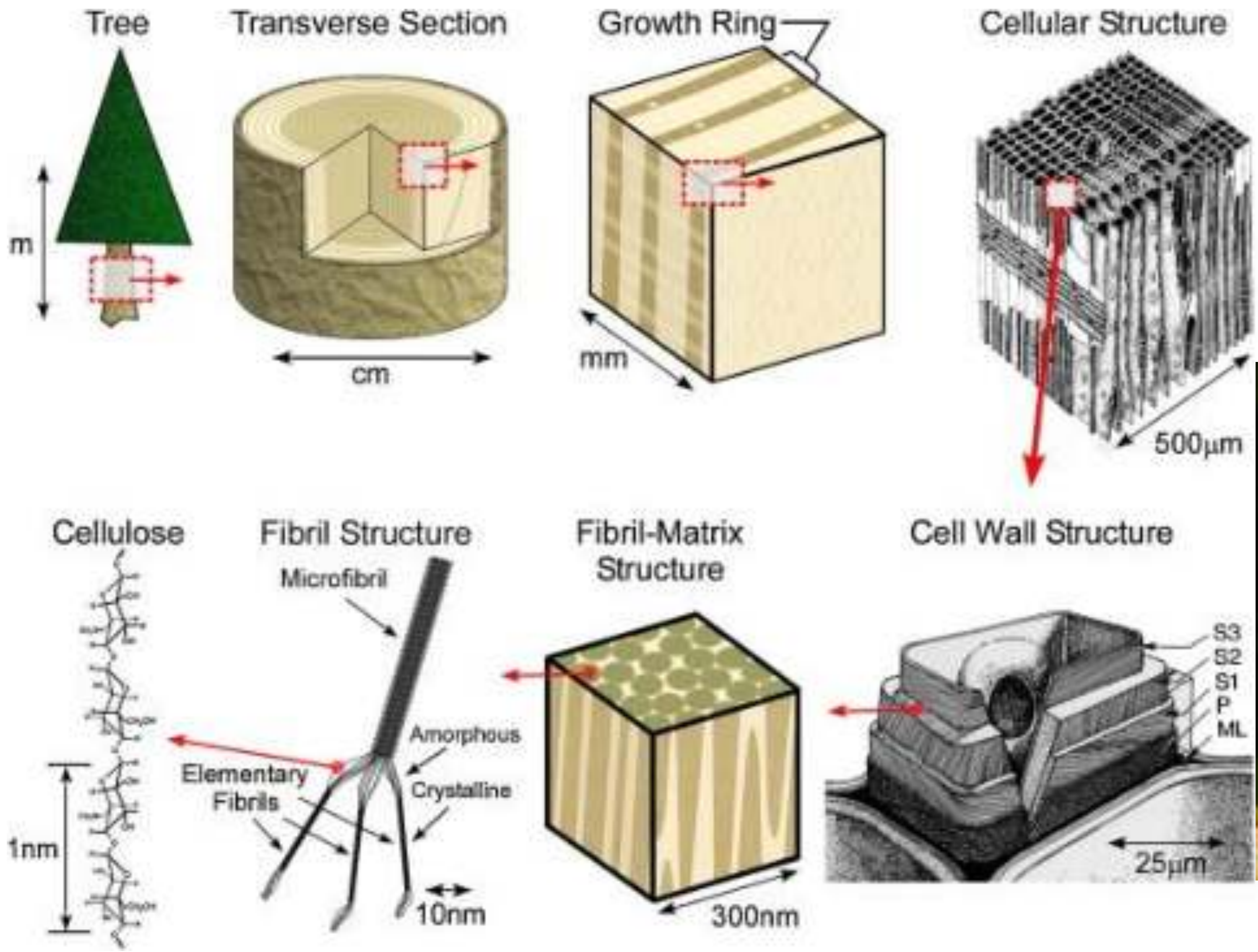
Photonic crystals

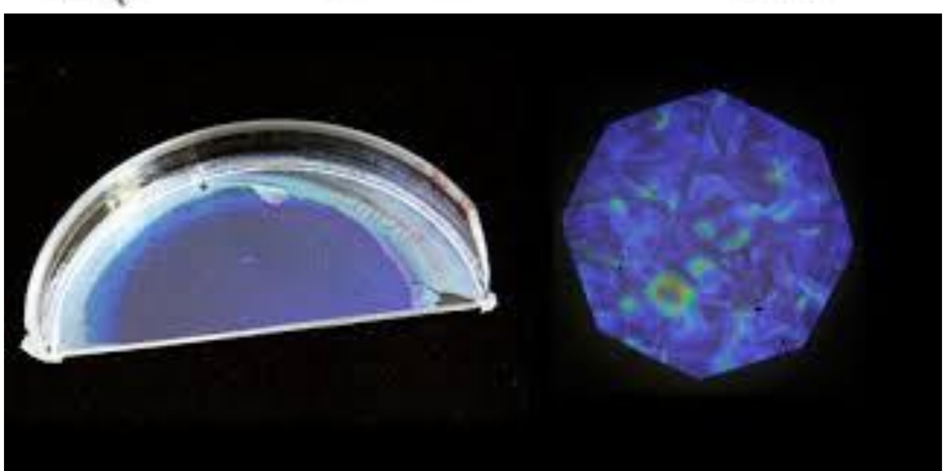
Received: 16 June 2014
Accepted: 22 January 2015
Published online: 10 March 2015



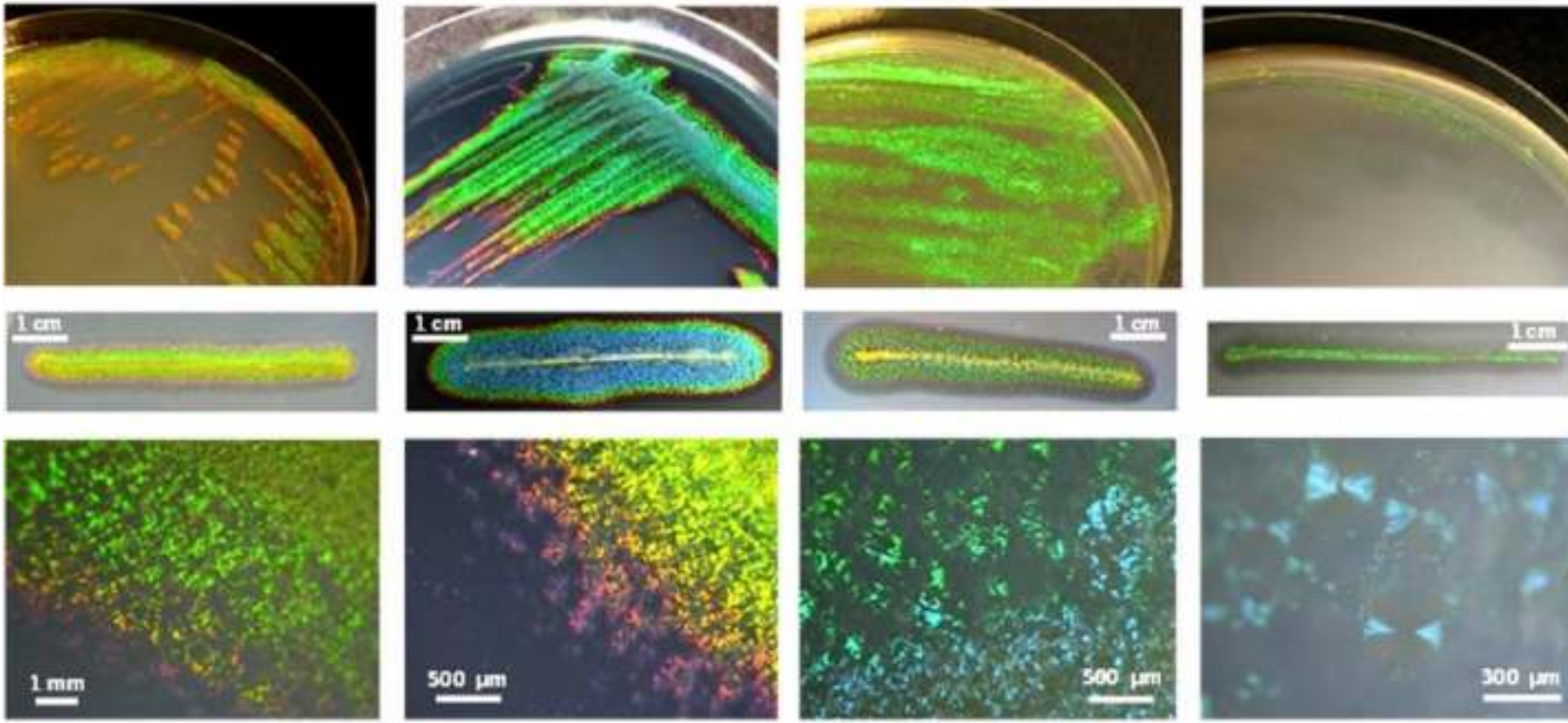
Chameleons can change their color in less than 1 second



The most intense blue known in nature: African Pollia condensata berries



Dumanli, A. G., Kamita, G., Landman, J., van der Kooij, H., Glover, B. J., Baumberg, J. J., Steiner, U. and Vignolini, S. (2014), "Controlled, Bio-inspired Self-Assembly of Cellulose-Based Chiral Reflectors." Advanced Optical Materials. doi: 10.1002/adom.201400112



SCIENTIFIC REPORTS

OPEN

A unique self-organization of bacterial sub-communities creates iridescence in *Cellulophaga lytica* colony biofilms

Received: 30 July 2015
Accepted: 17 December 2015
Published: 28 January 2016

Betty Kientz[1,*], Stephen Luke[2], Peter Vukusic[2,*], Renaud Péteri[3,*], Cyrille Beaudry[3], Tristan Renault[4], David Simon[3], Tâm Mignot[5] & Eric Rosenfeld[1,*]

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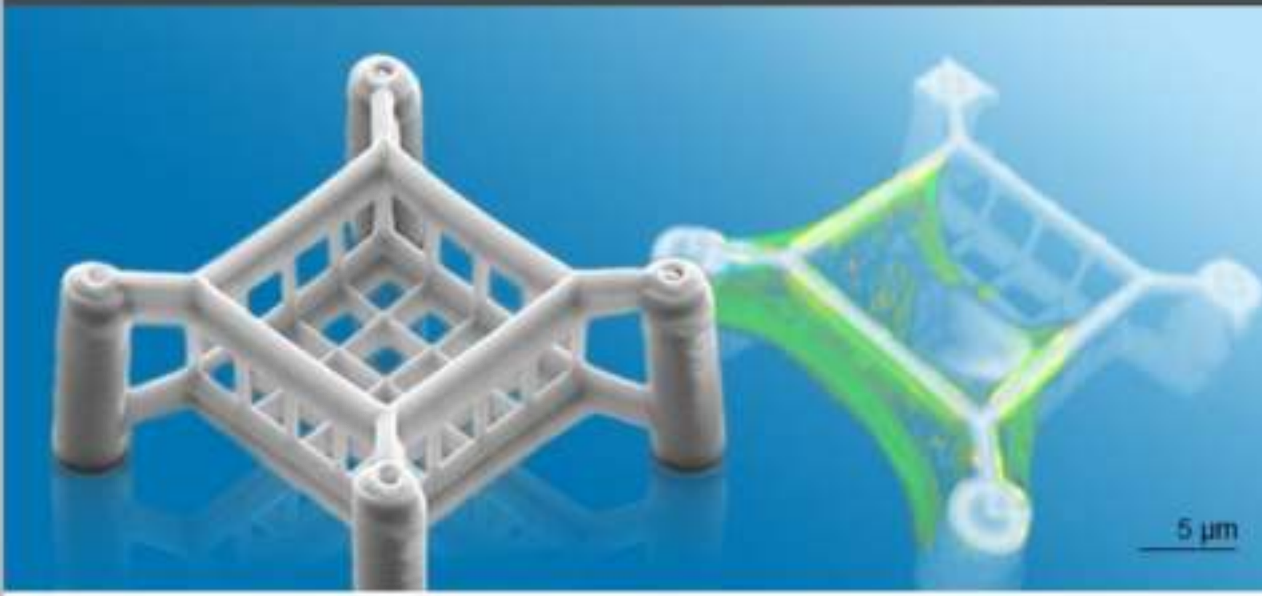

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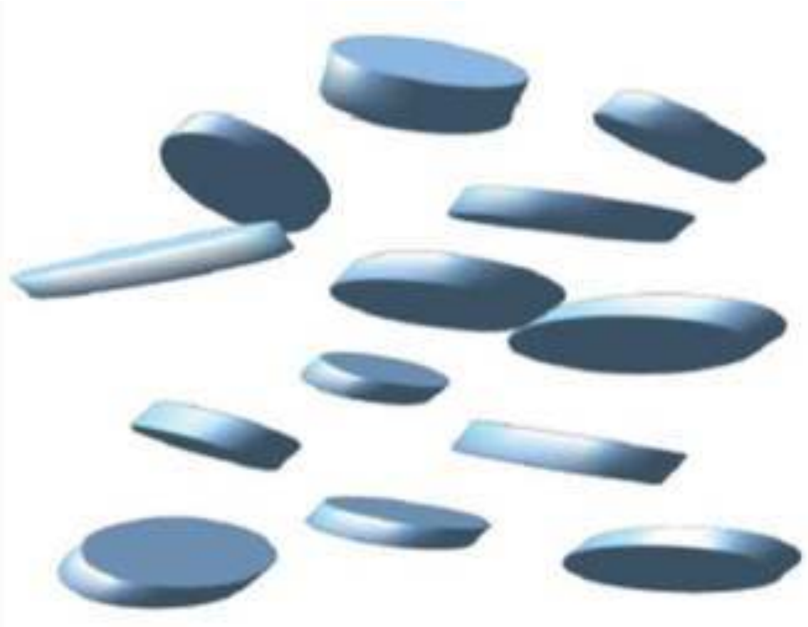
Self-assembly:

Making a macroscopic sample (i.e. about 10^{20} nanoparticles) by physically picking up and moving nanoparticles into place, one by one, would take about 300 million years, even if the time for moving individual particles could be made as short as 1 millisecond.



1896. ANNALEN DER PHYSIK UND CHEMIE. № 11.

NEUE FOLGE. BAND 59.

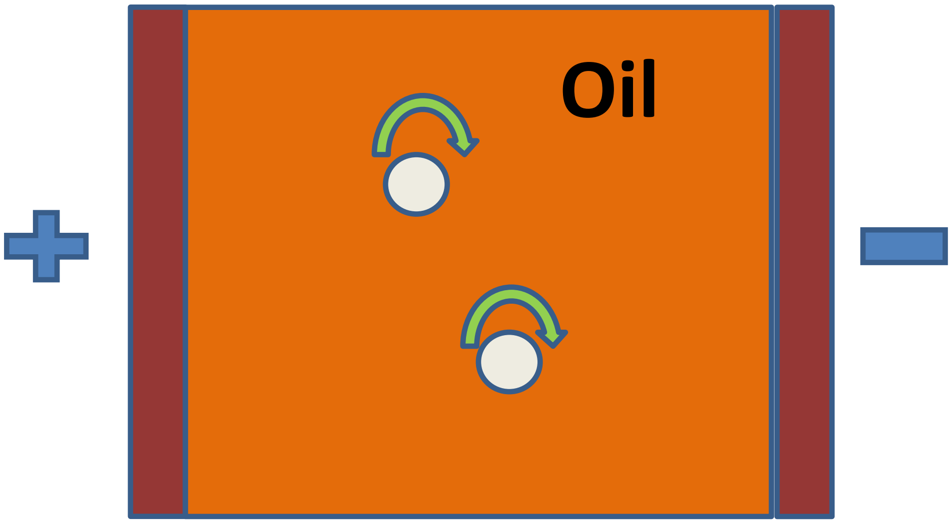
1. *Ueber Rotationen im constanten electrischen Felde; von G. Quincke.*[1]

(Hierzu Taf. V u. VI Fig. 1—28.)

Georg Hermann Quincke

Born	19 November 1834 Frankfurt (Oder)
Died	13 January 1924 (aged 89) Heidelberg
Nationality	German
Fields	Physics
Doctoral advisor	H. G. Magnus, F. E. Neumann
Doctoral students	K. F. Braun, P. Lenard

Quincke rotation



Small glass beads rotate spontaneously when immersed in liquids and subject to an electrostatic field

1. Threshold electric field
2. Rotation axis normal to the applied E-field

Quincke rotation

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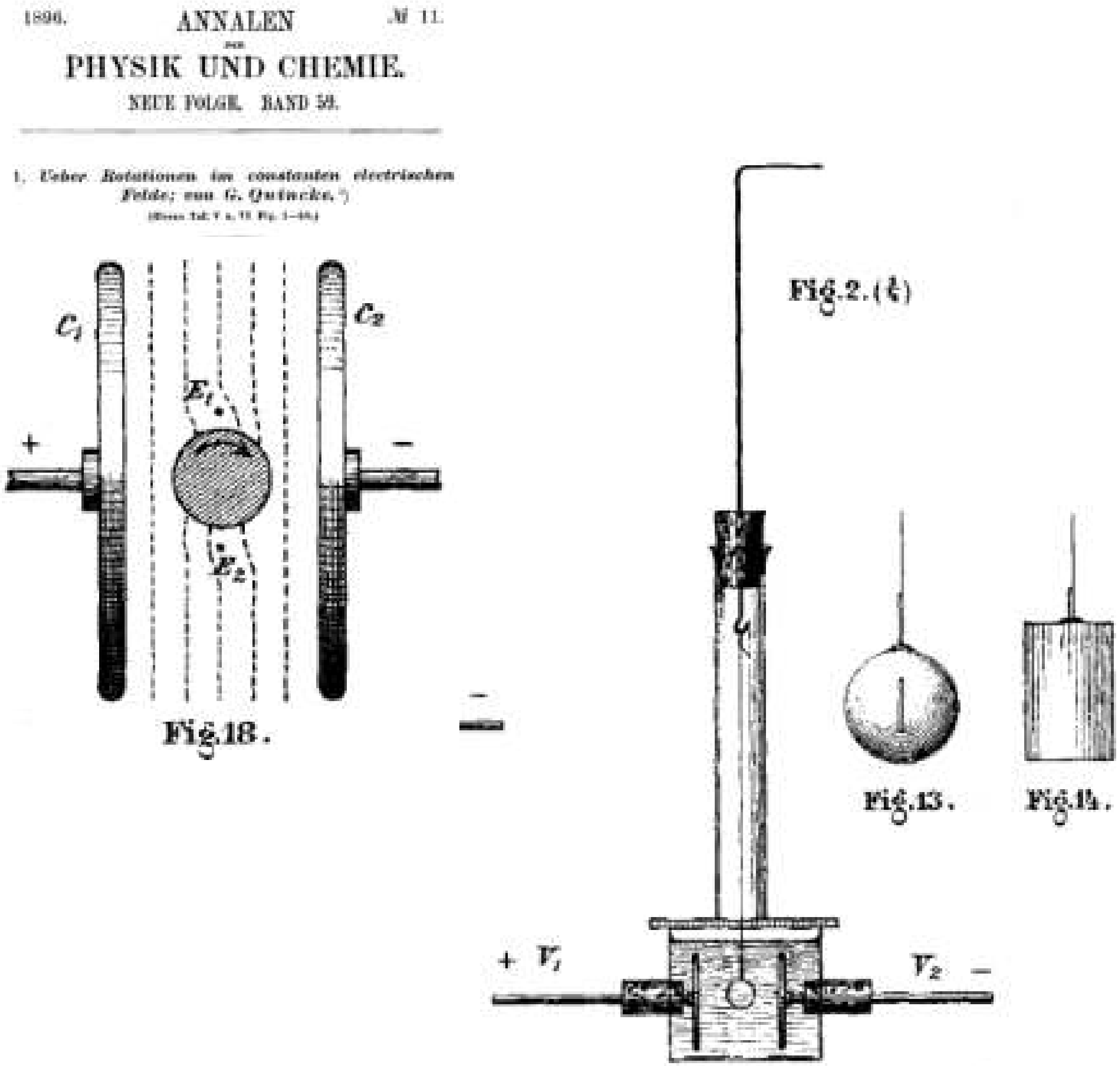

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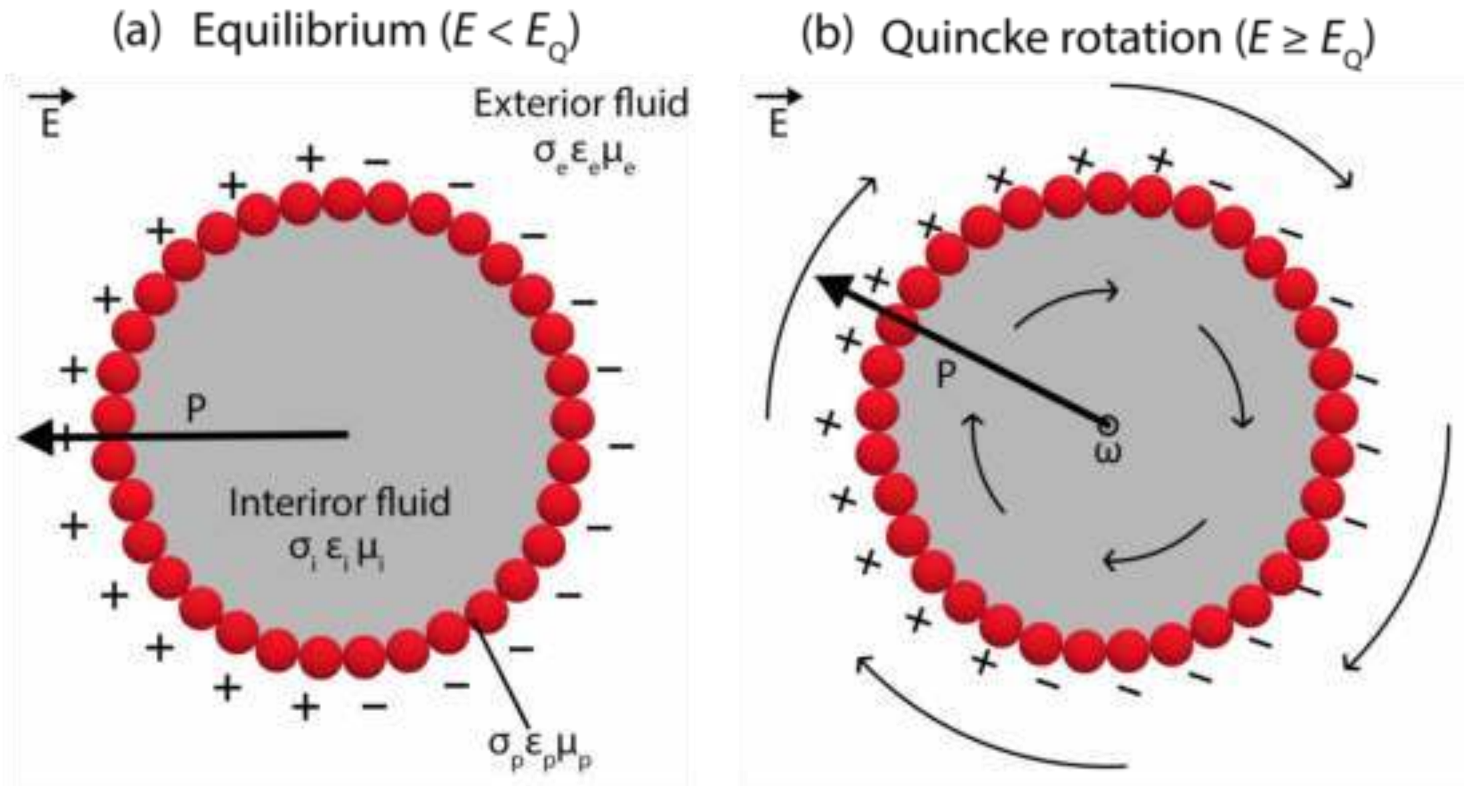
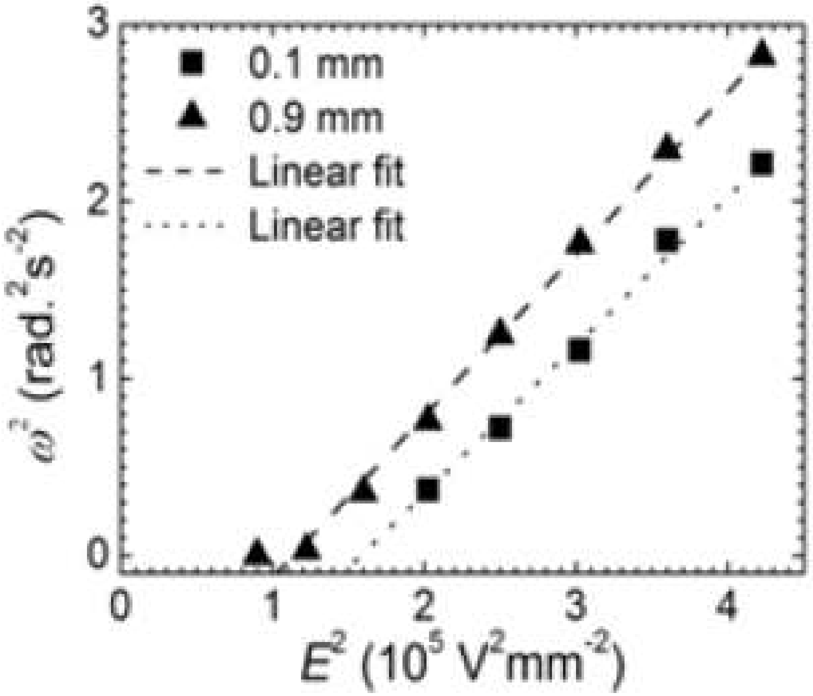


Quincke rotation of Pickering frops. Experiments at NTNU Trondheim

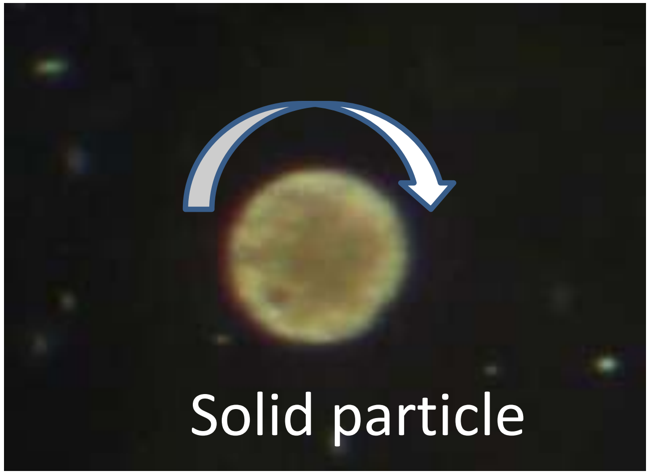
Movie of single Quincke rotating Pickering drop

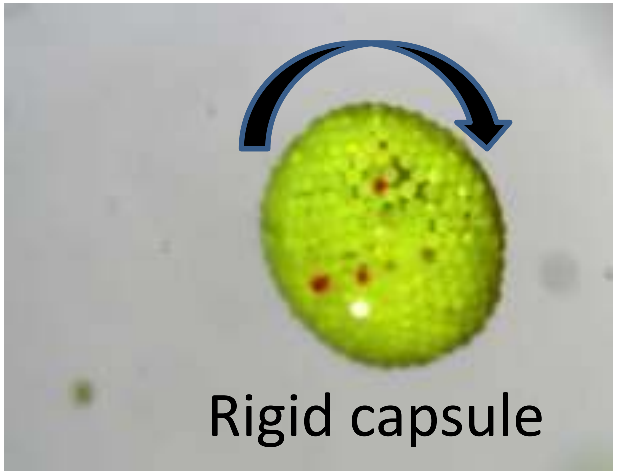
Quincke rotation of Pickering drops. Experiments at NTNU Trondheim



$$\Omega = \pm \frac{1}{\tau_{\mathrm{MW}}} \sqrt{\left(\frac{E_e}{E_c}\right)^2 - 1}, \quad \text{with}$$

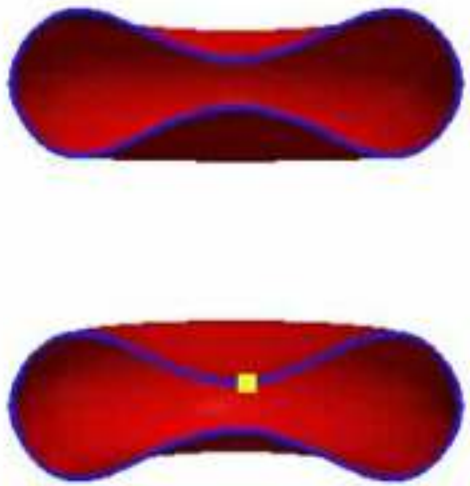
$$E_c = \sqrt{\frac{2\eta}{\varepsilon_1 \tau_{\mathrm{MW}}(\varepsilon_{21} - \sigma_{21})}}.$$





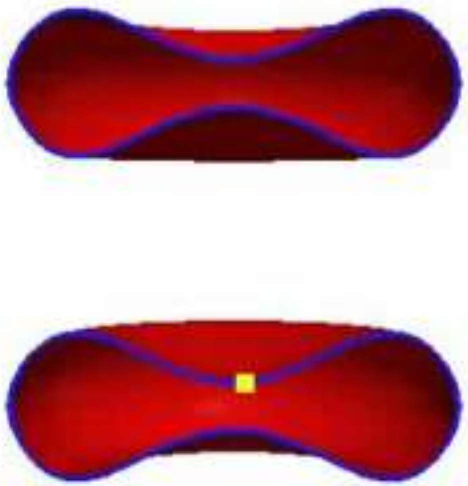
Quincke rotation of Pickering drops. Experiments at NTNU Trondheim

Tank treading and tumbling motion

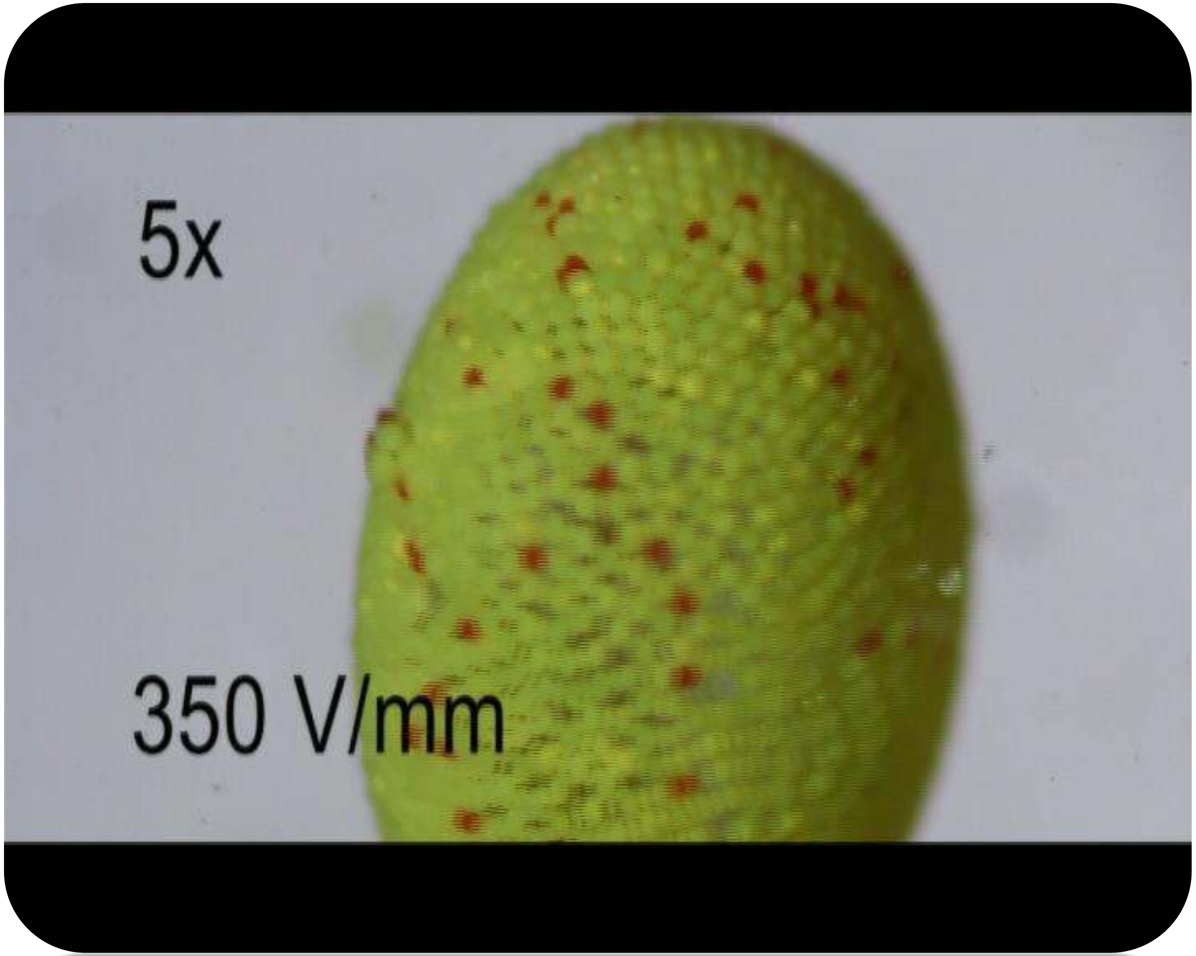


Video from: http://www.youtube.com/watch?v=mKLhfb5csr4

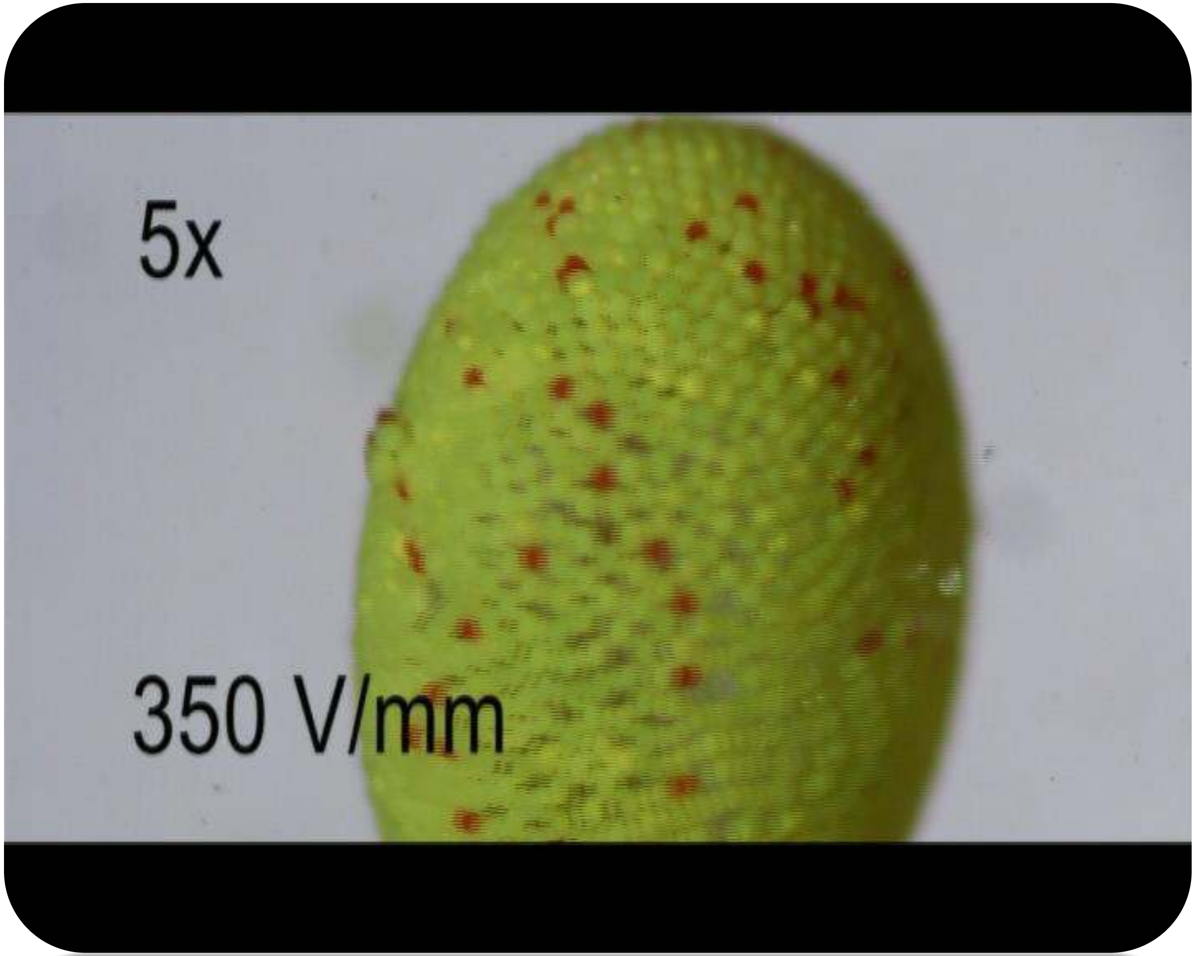
Tumbling and tank treading motion



Video from: http://www.youtube.com/watch?v=mKLhfb5csr4

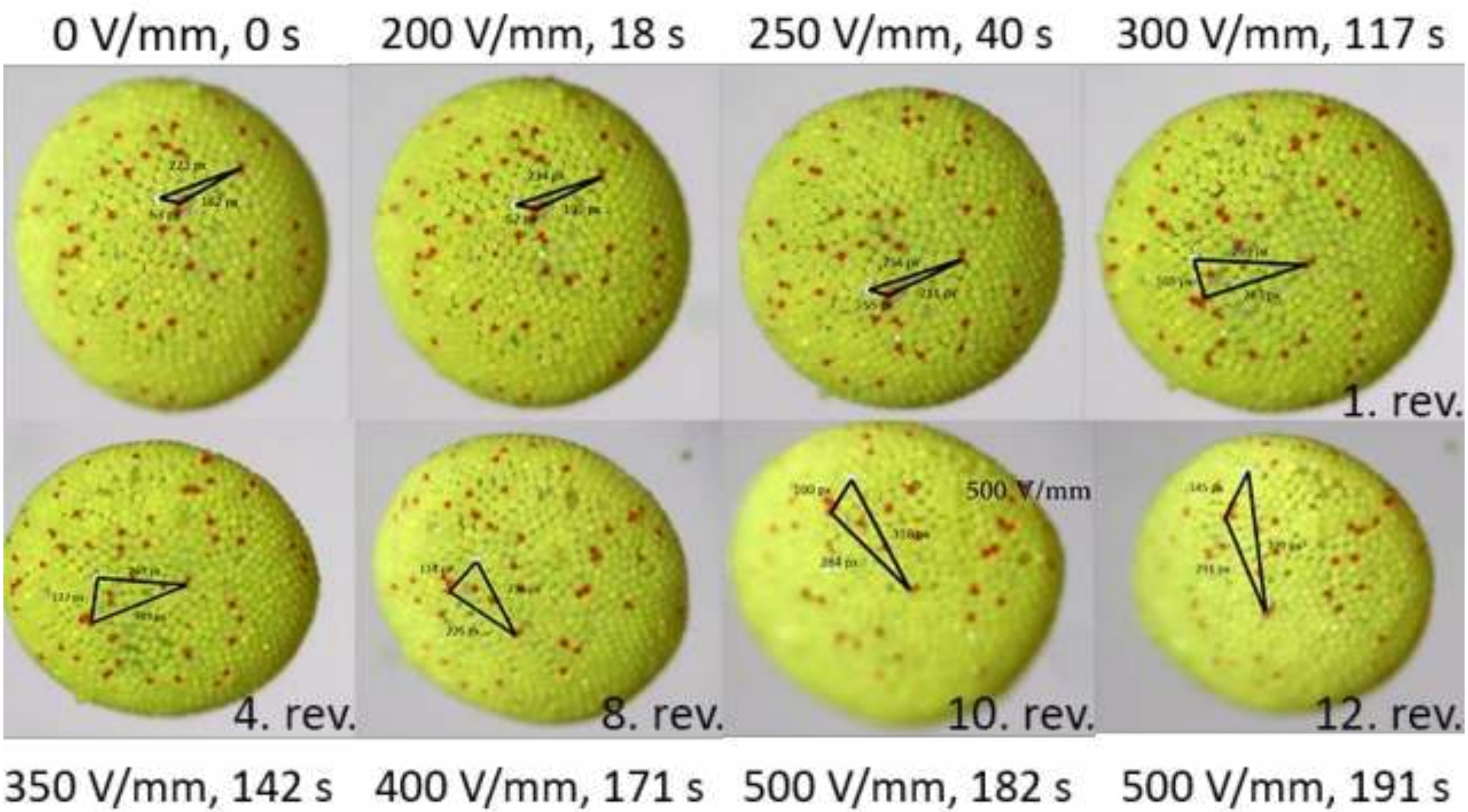


Transition from solid shell rotation to **tank treading: Experiments at NTNU Trondheim**

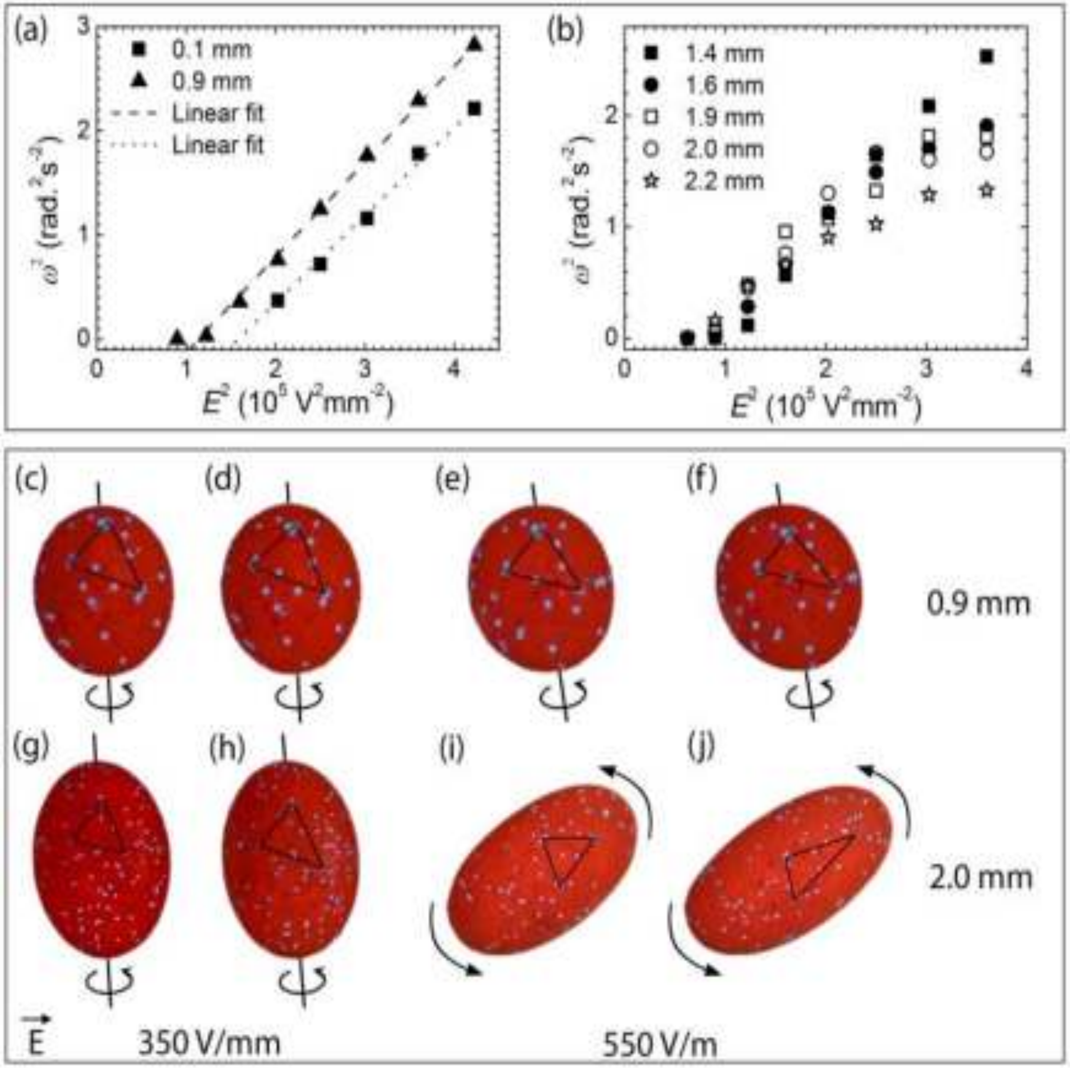


Transition from solid shell rotation to **tank treading:**
Experiments at NTNU Trondheim

Particle tracking

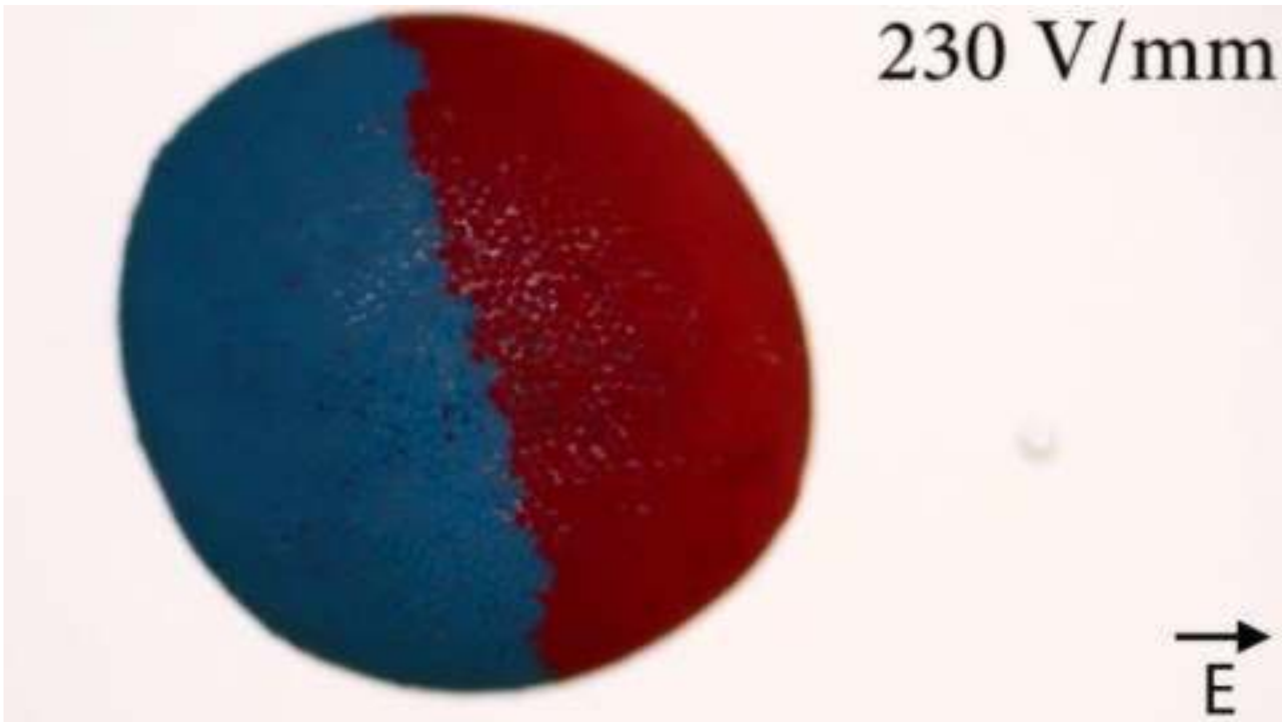


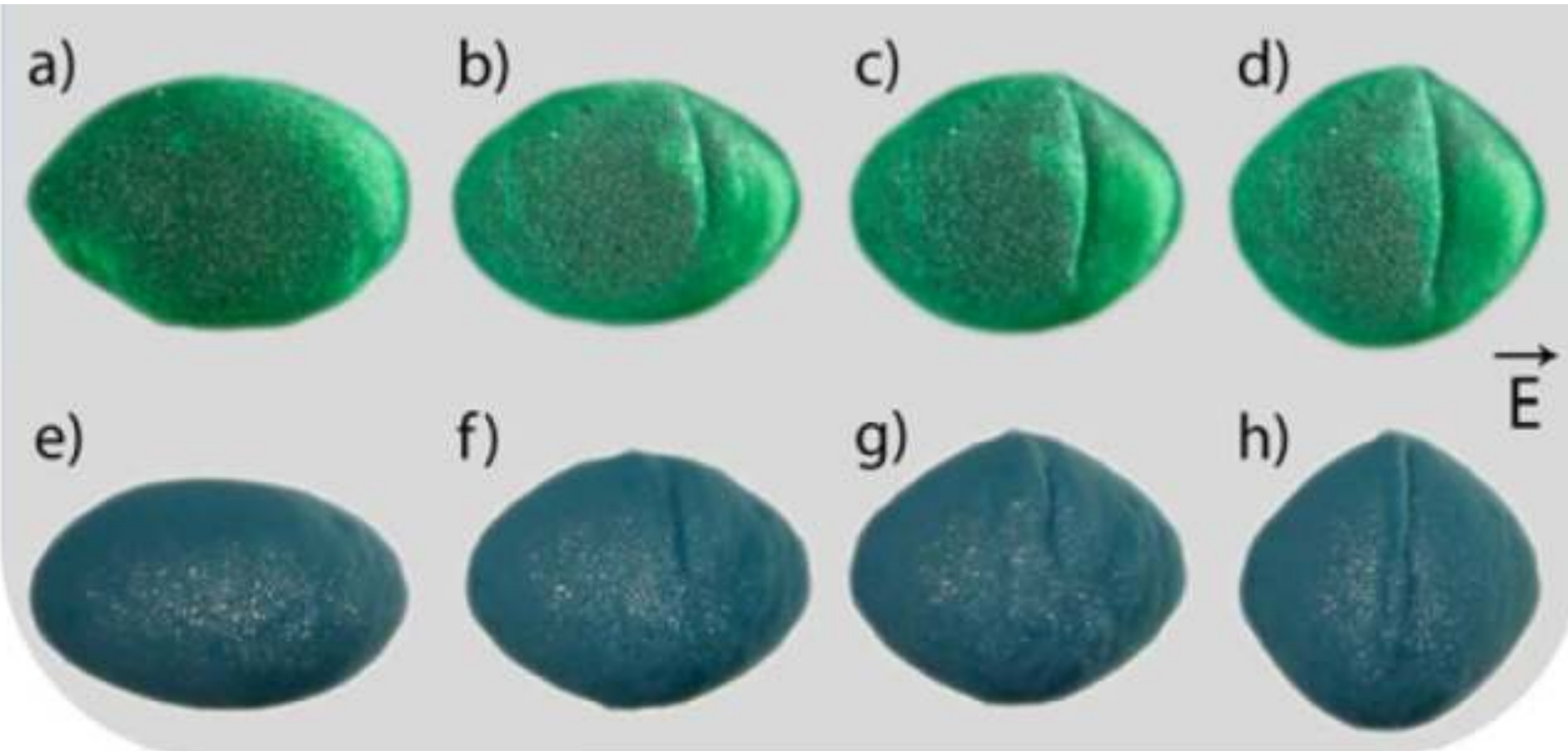
Transition from solid shell rotation to **tank treading:**
Experiments at NTNU Trondheim



Transition from solid shell rotation to **tank treading:**
Experiments at NTNU Trondheim

Solid to liquid transition of the particle layer occurs when we increase the E-field





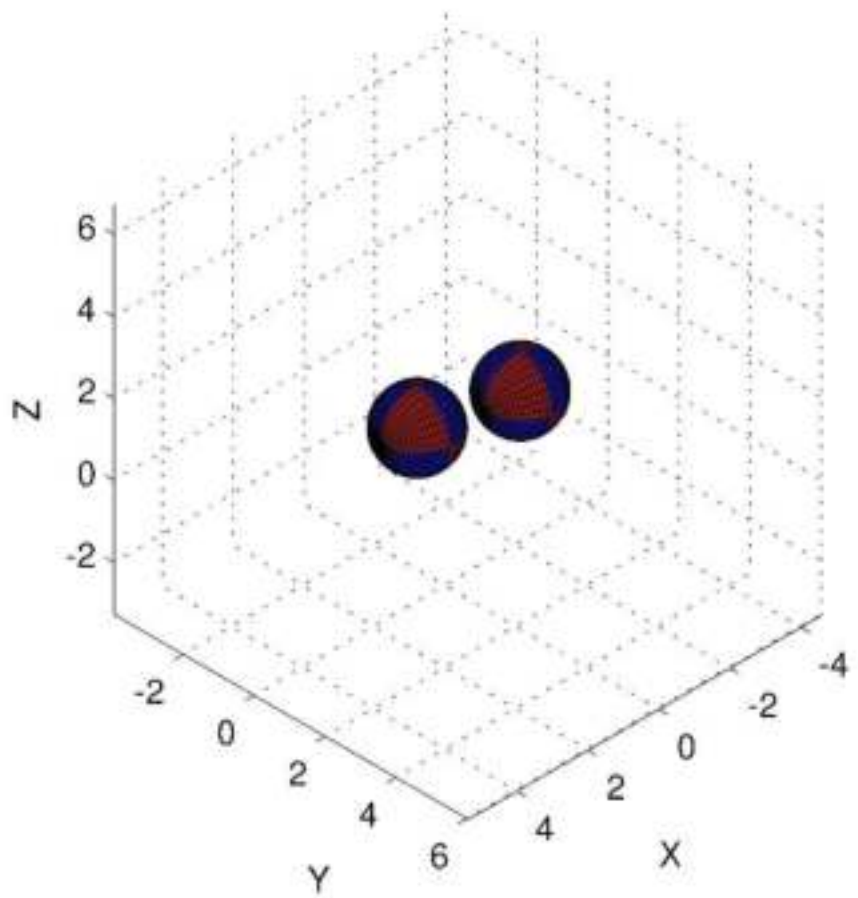
Electrobuckling: Experiments at NTNU Trondheim

Crumpling

PHYSICAL REVIEW E 87, 043014 (2013)

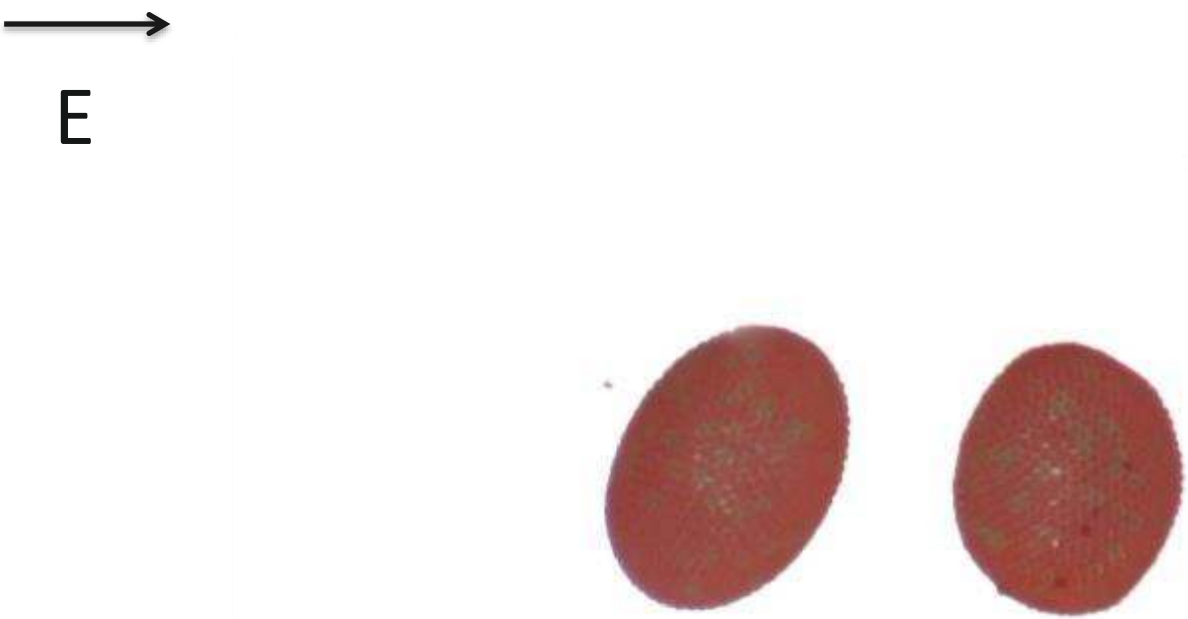
Electrohydrodynamic interaction of spherical particles under Quincke rotation

Debasish Das and David Saintillan*
Department of Mechanical Science and Engineering, University of Illinois at Urbana-Champaign, Urbana, Illinois 61801, USA
(Received 3 March 2013; published 29 April 2013)



Interaction of Quincke rotating beads

Swimming Quincke rotating Pickering pair



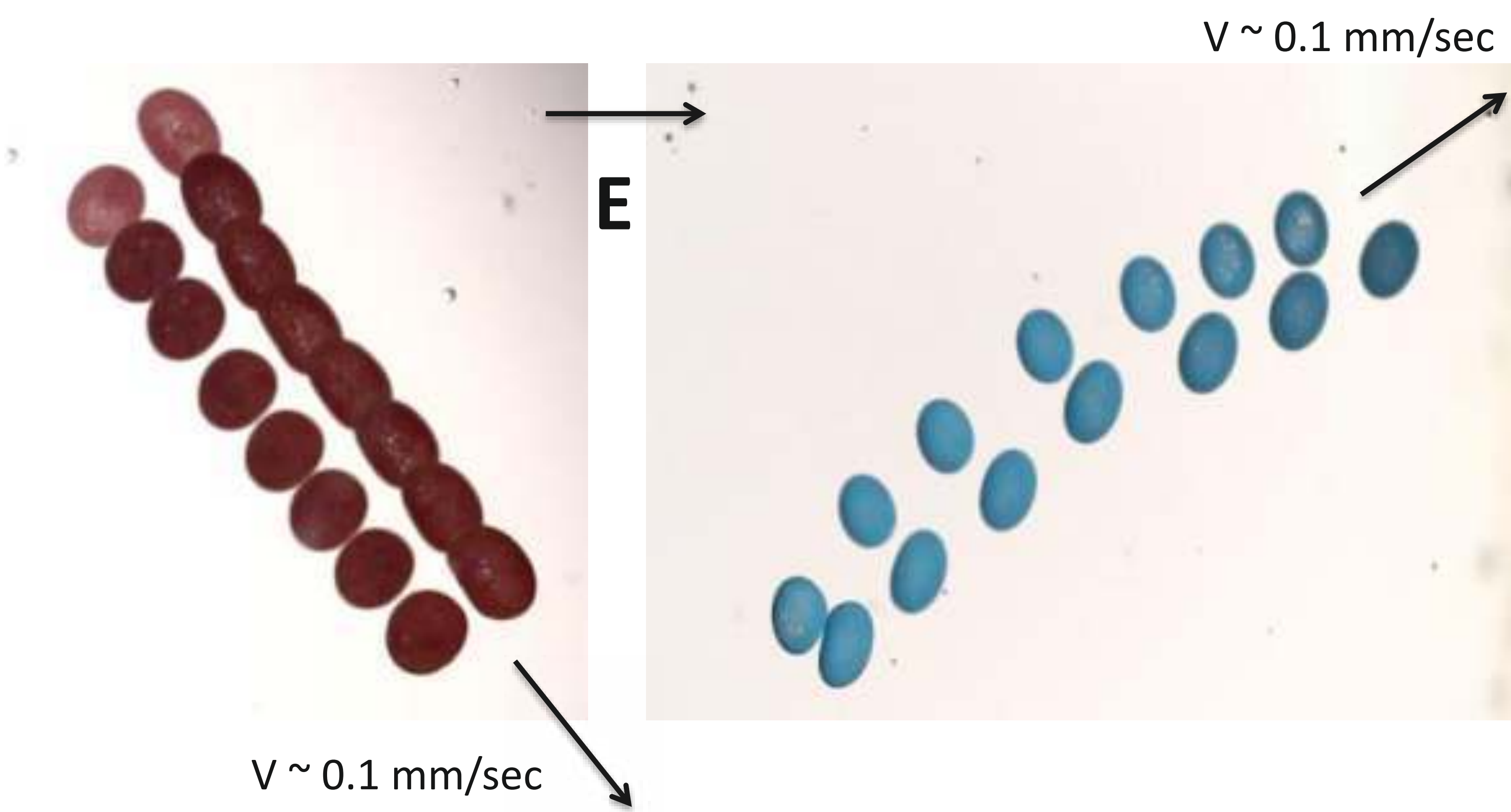
Experiments at NTNU Trondheim

Swimming upwards

- E

Experiments at NTNU Trondheim

Pair swimming of tank treading capsules



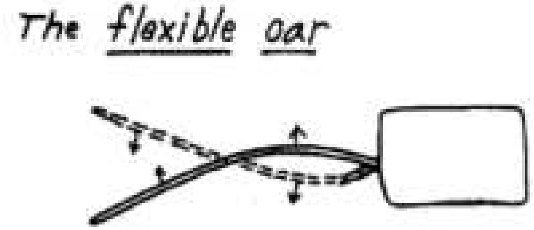
Experiments at NTNU Trondheim

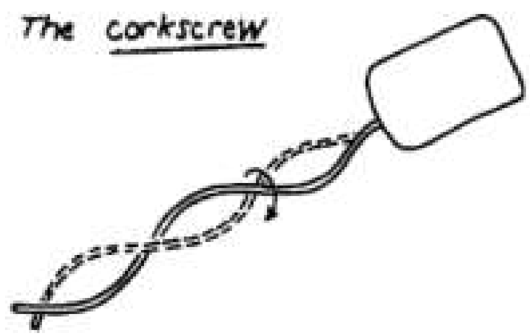
Electro-hydrodynamic propulsion of counter-rotating Pickering drops P. Dommersnes, A. Mikkelsen & J. O. Fossum EUROPEAN PHYSICAL JOURNAL SPECIAL TOPICS 225, 699-705 (2016)

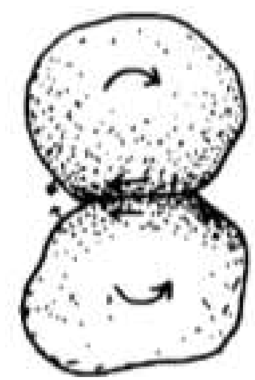
Life at low Reynolds number American Journal of Physics, Vol. 45, No. 1, January 1977

E. M. Purcell
Lyman Laboratory, Harvard University, Cambridge, Massachusetts 02138
(Received 12 June 1976)

Another animal might consist of two cells which were stuck together and were able to roll on one another by having some kind of attraction here while releasing there. That thing will "roll" along.







Counter-rotating rotors

Swimmers

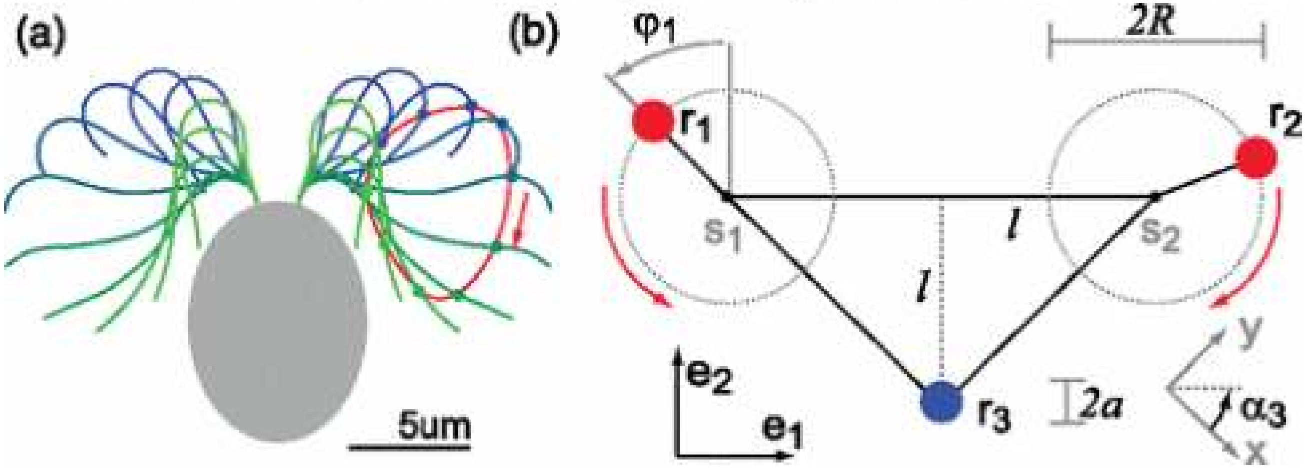
Chlamydomonas is a single-cell green alga about 10 micrometres in diameter that swims with two flagella.

Two-rotor bifilament swimmer: Chlamydomonas

Selected for a Viewpoint in *Physics*
PRL **109,** 138102 (2012) PHYSICAL REVIEW LETTERS week ending 28 SEPTEMBER 2012

Flagellar Synchronization Independent of Hydrodynamic Interactions

Benjamin M. Friedrich[*] and Frank Jülicher
Max Planck Institute for the Physics of Complex Systems, Nöthnitzer Straße 38, 01187 Dresden, Germany
(Received 7 June 2012; published 24 September 2012)



New Journal of Physics
The open access journal for physics

Phase-dependent forcing and synchronization in the three-sphere model of *Chlamydomonas*

Rachel R Bennett and Ramin Golestanian[1]
Rudolf Peierls Center for Theoretical Physics, University of Oxford, Oxford OX1 3NP, UK
E-mail: ramin.golestanian@physics.ox.ac.uk

New Journal of Physics **15** (2013) 075028 (17pp)
Received 10 April 2013
Published 30 July 2013
Online at http://www.njp.org/
doi:10.1088/1367-2630/15/7/075028

Two-rotor model of bifilament swimmer

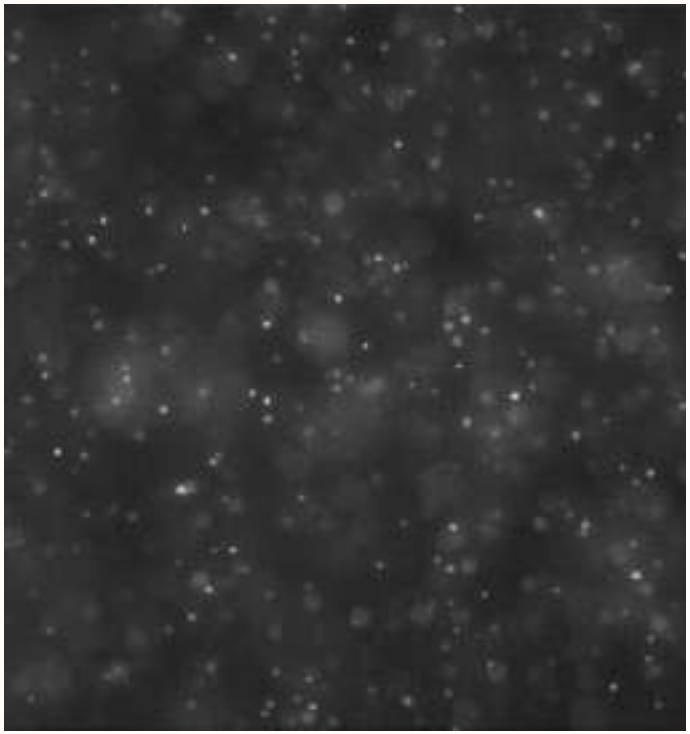


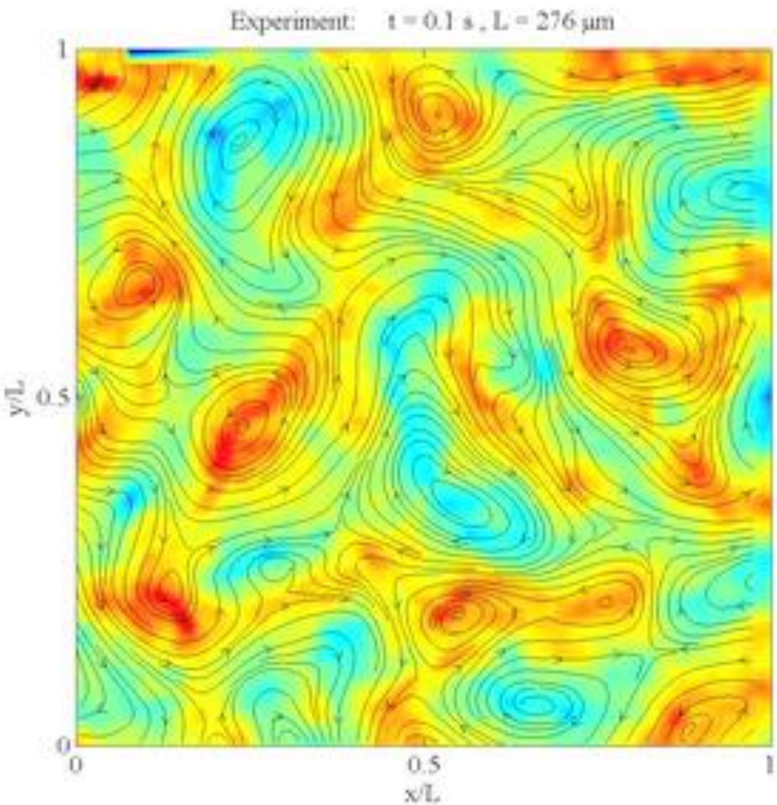

Flocking and swarming

Selected for a Viewpoint in *Physics*
PRL **110,** 228102 (2013) PHYSICAL REVIEW LETTERS week ending 31 MAY 2013

Fluid Dynamics of Bacterial Turbulence

Jörn Dunkel,[1] Sebastian Heidenreich,[2] Knut Drescher,[3] Henricus H. Wensink,[4] Markus Bär,[2] and Raymond E. Goldstein[1]



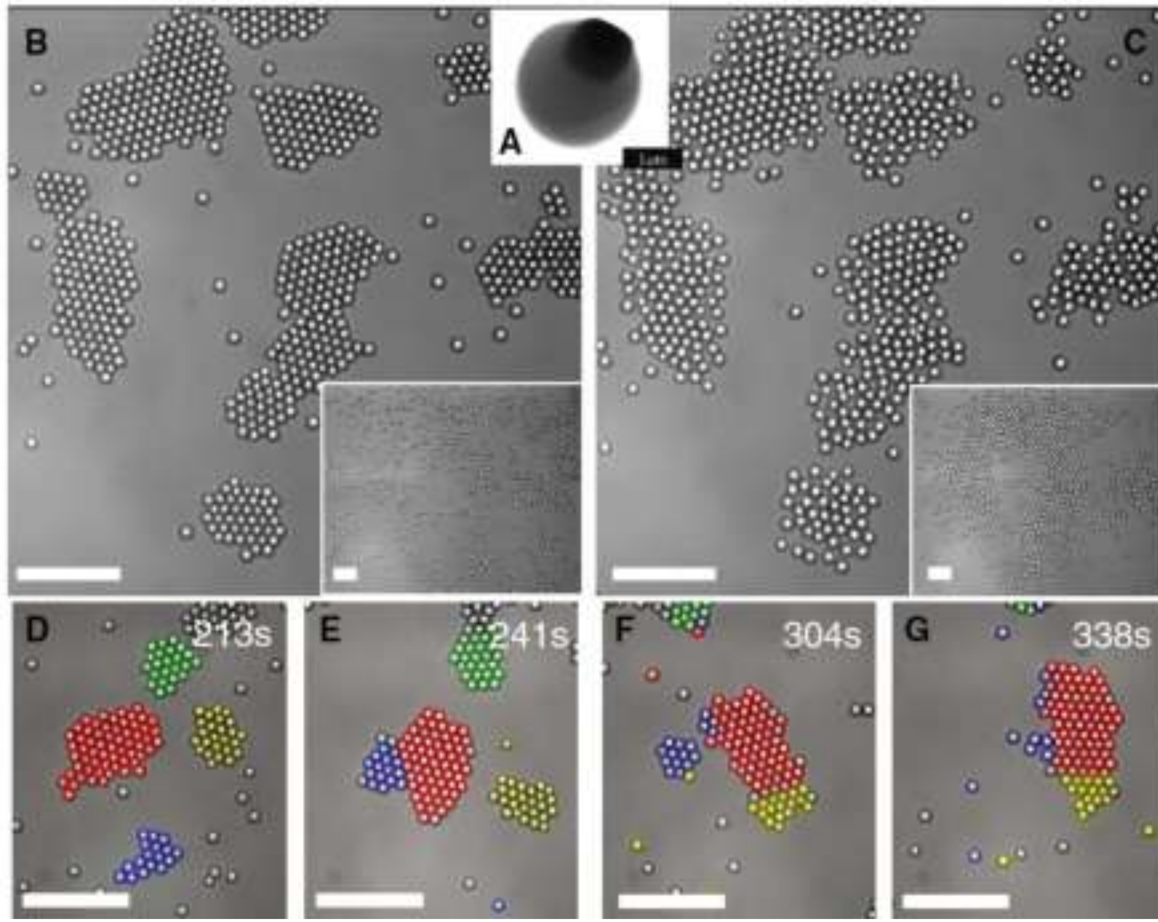


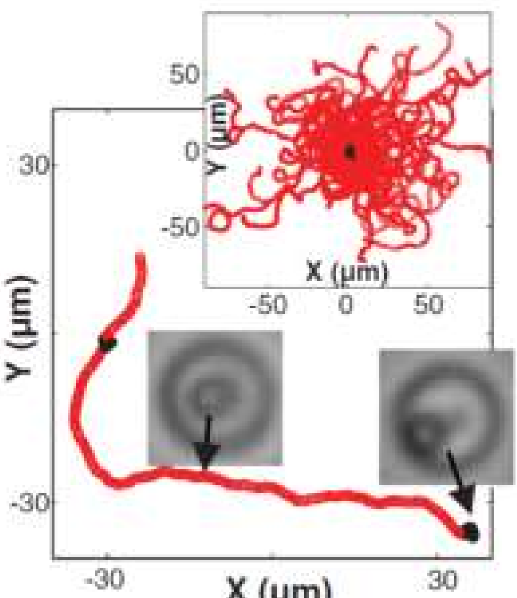
Living Crystals of Light-Activated Colloidal Surfers

Jeremie Palacci *et al.*

Science **339**, 936 (2013);
DOI: 10.1126/science.1230020

Fig. 1. (**A**) Scanning electron microscopy (SEM) of the bimaterial colloid: a TPM polymer colloidal sphere with protruding hematite cube (dark). (**B**) Living crystals assembled from a homogeneous distribution (inset) under illumination by blue light. (**C**) Living crystals melt by thermal diffusion when light is extinguished: Image shows system 10 s after blue light is turned off (inset, after 100 s). (**D** to **G**) The false colors show the time evolution of particles belonging to different clusters. The clusters are not static but rearrange, exchange particles, merge (D→F), break apart (E→F), or become unstable and explode (blue cluster, F→G). For (B) to (G), the scale bars indicate 10 μm. The solid area fraction is $\Phi_s \approx 0.14$.





A hematite cube protruding from a TPM polymer spheremoves on fixed glass substrate when exposed to blue light (red part of trace) and diffuses when the light is off (black part of trace). Initially, with no light, the hematite cube is oriented randomly (image, right) but rotates and faces downward toward the glass substrate when the light is turned on (image, left). The particle then surfs on the osmotic flow it induces between the substrate and itself. (Inset) A superposition of the trajectories of many particles with their origins aligned.

Living Crystals of Light-Activated Colloidal Surfers
Jeremie Palacci *et al.*
Science **339**, 936 (2013);
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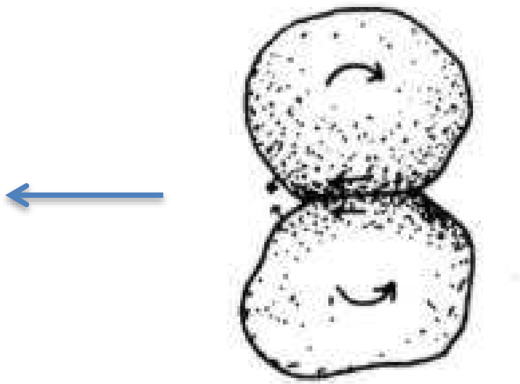
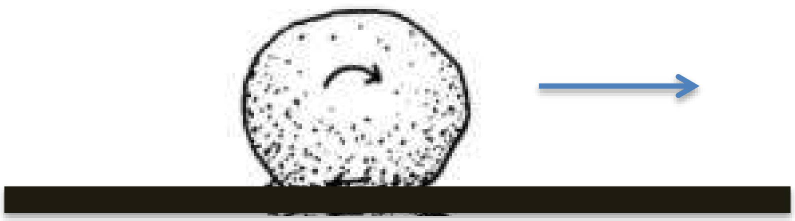
Phoretic and osmotic effects can conveniently be switched on and off by light.

Pair rollers

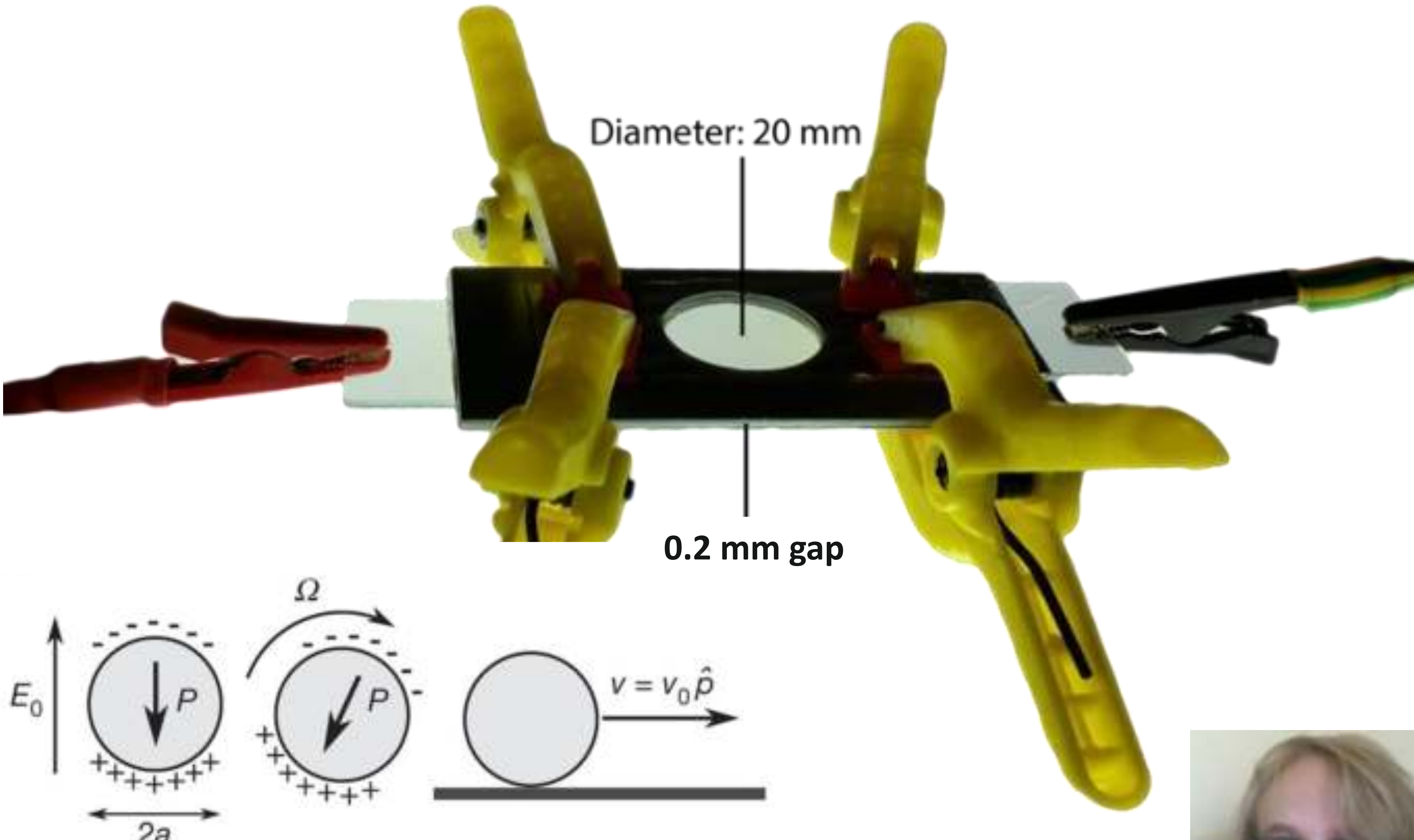


Surface roller



Kicking off one another, or kicking of a surface

Hele-Shaw cell with ITO glass covers: suspension containg 30micron PS beads



Experiments at NTNU Trondheim: Tommy Kristiansen

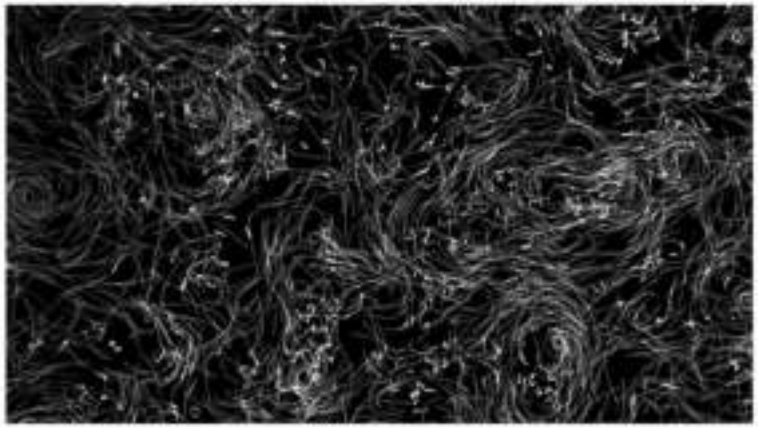
40µm 2250V/mm

Fast moving quincke rollers

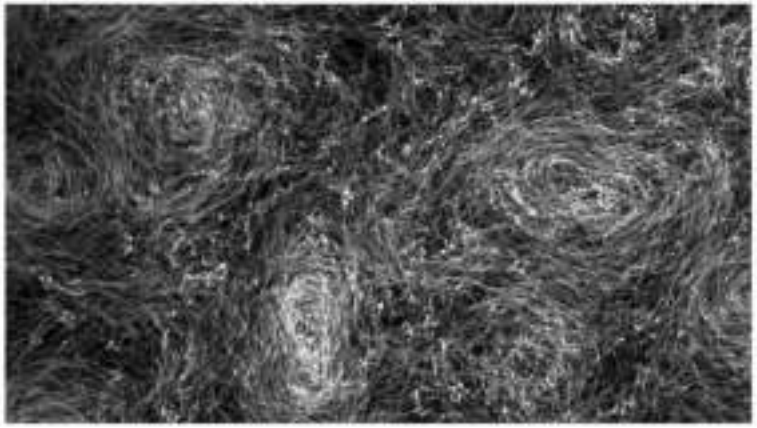
Experiments at NTNU Trondheim: Tommy Kristiansen

Streak photography night sky

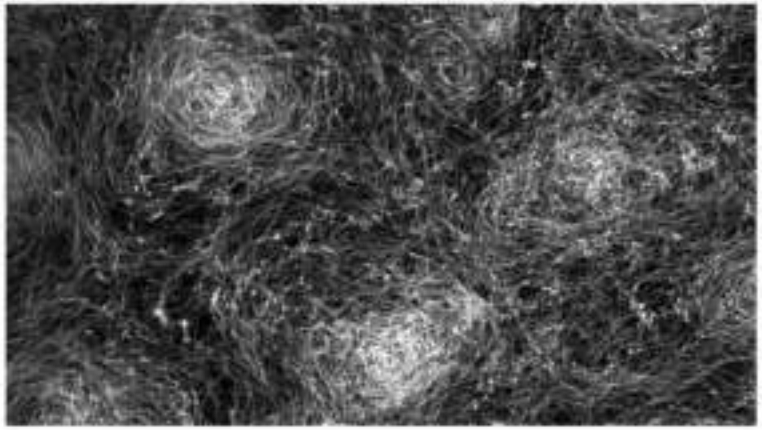
Streak photos of fast moving Quincke rollers: «Vortices»



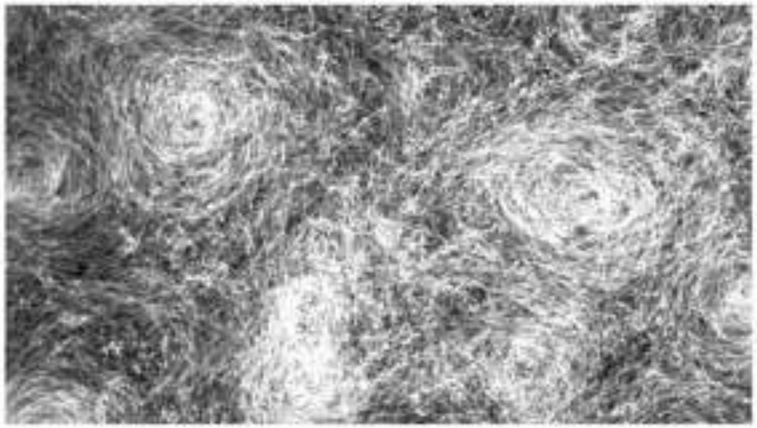
15 frames after 0 secs



100 frames after 3 secs

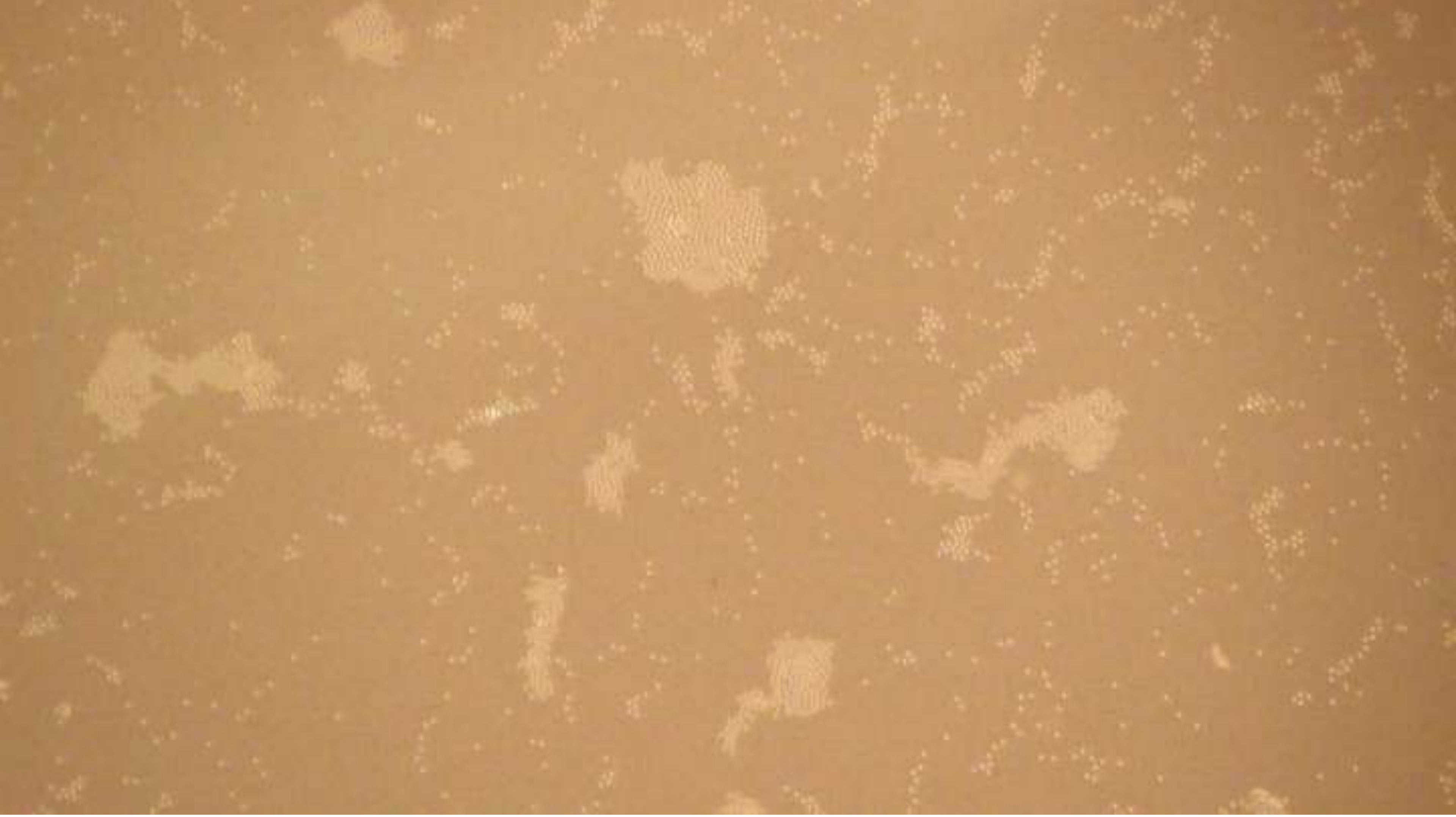


100 frames after 6 secs



100 frames after 9 secs

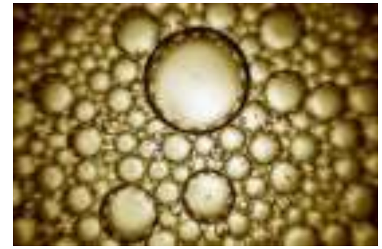
Experiments at NTNU Trondheim: Tommy Kristiansen



30µm 1375V/mm 60fps «Living crystals «or active «entangled matter»

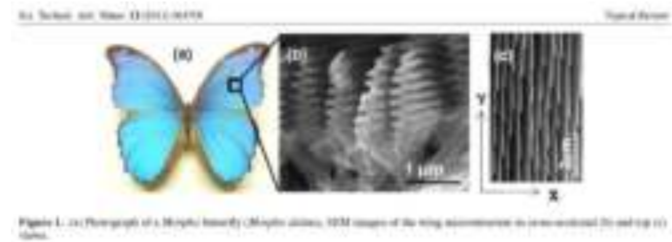
Experiments at NTNU Trondheim: Tommy Kristiansen

Enhanced Oil-Recovery by means of nanofluids
(Dept. of Petr. Eng. & Appl. Geophys. NTNU)

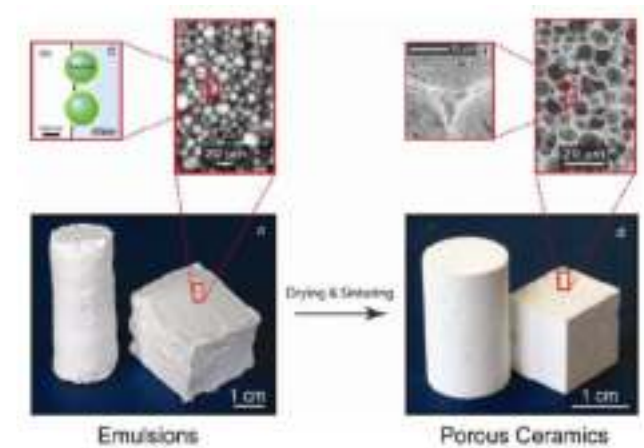


+ nanoparticles

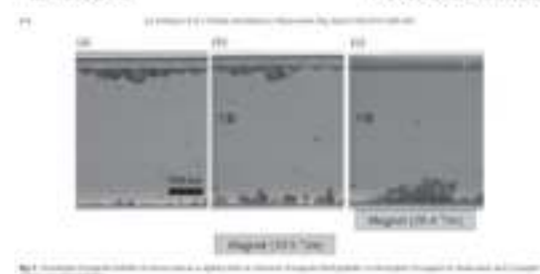
Structural colours: Biomimetic etc
(Dept. of Physics, NTNU)



Pickering foams for new construction materials
(Dept. of Physics, NTNU)



Magnetic control of Pickering drops
(Dept. of Physics, NTNU)



Curiosity driven research

«HEY, SÀM, THE BIG ROUND YELLOW THING CAME UP AGAIN»

Thank you for your attention!

"This could be the discovery of the century. Depending, of course, on how far down it goes."

Questions?