"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

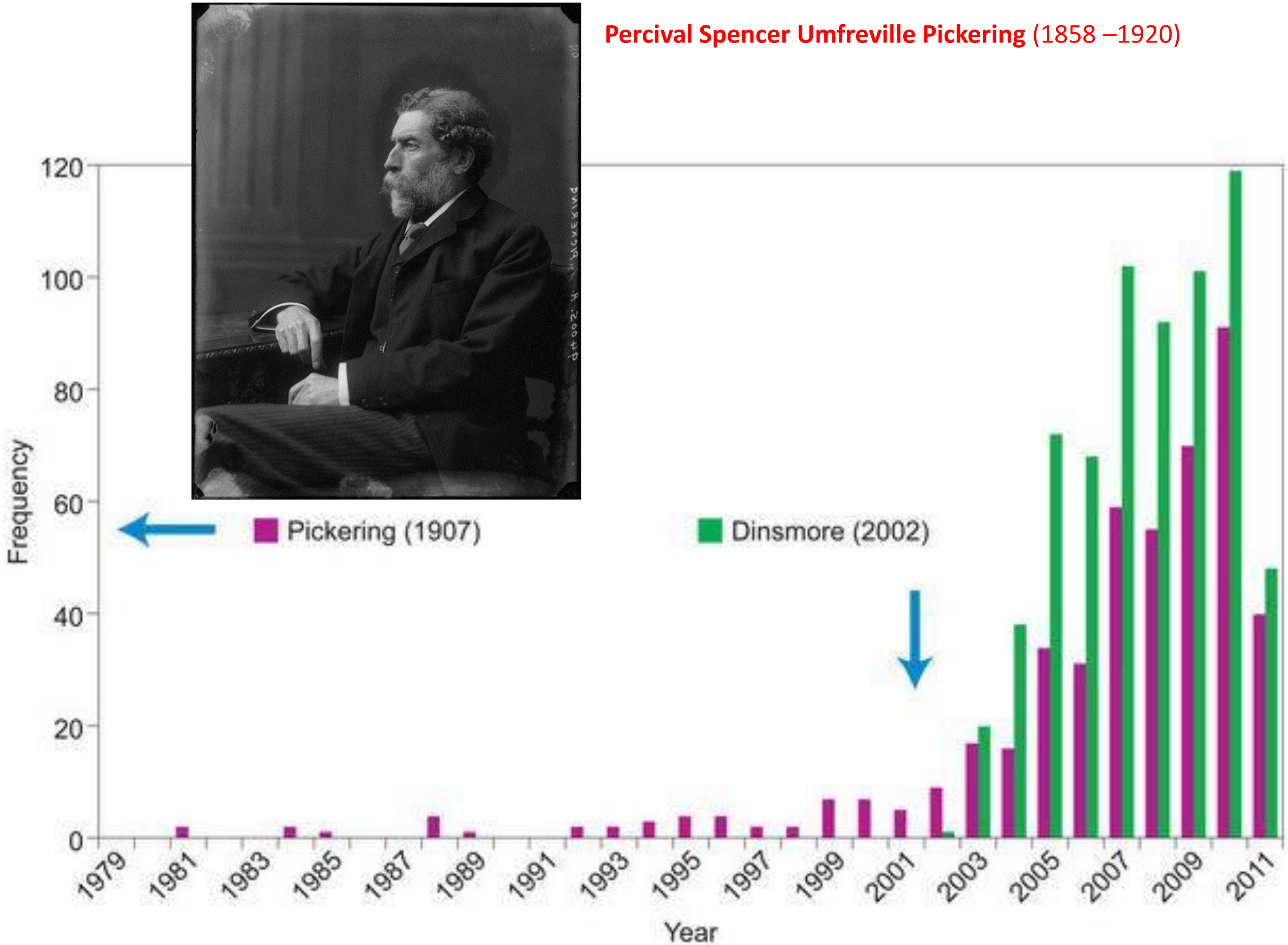
CXCVI.—*Emulsions.*

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)

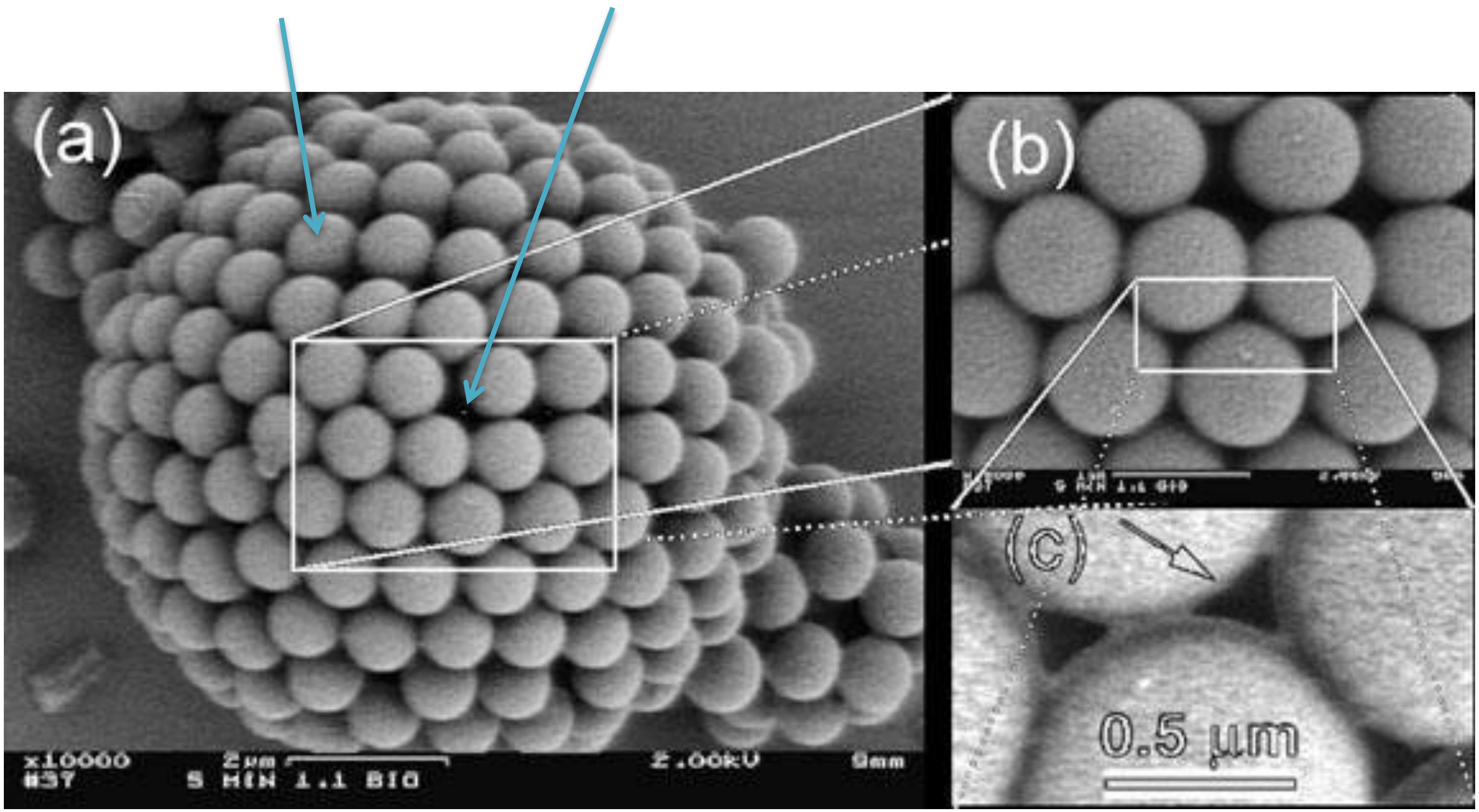
Percival Spencer Umfreville Pickering (1858 –1920)



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

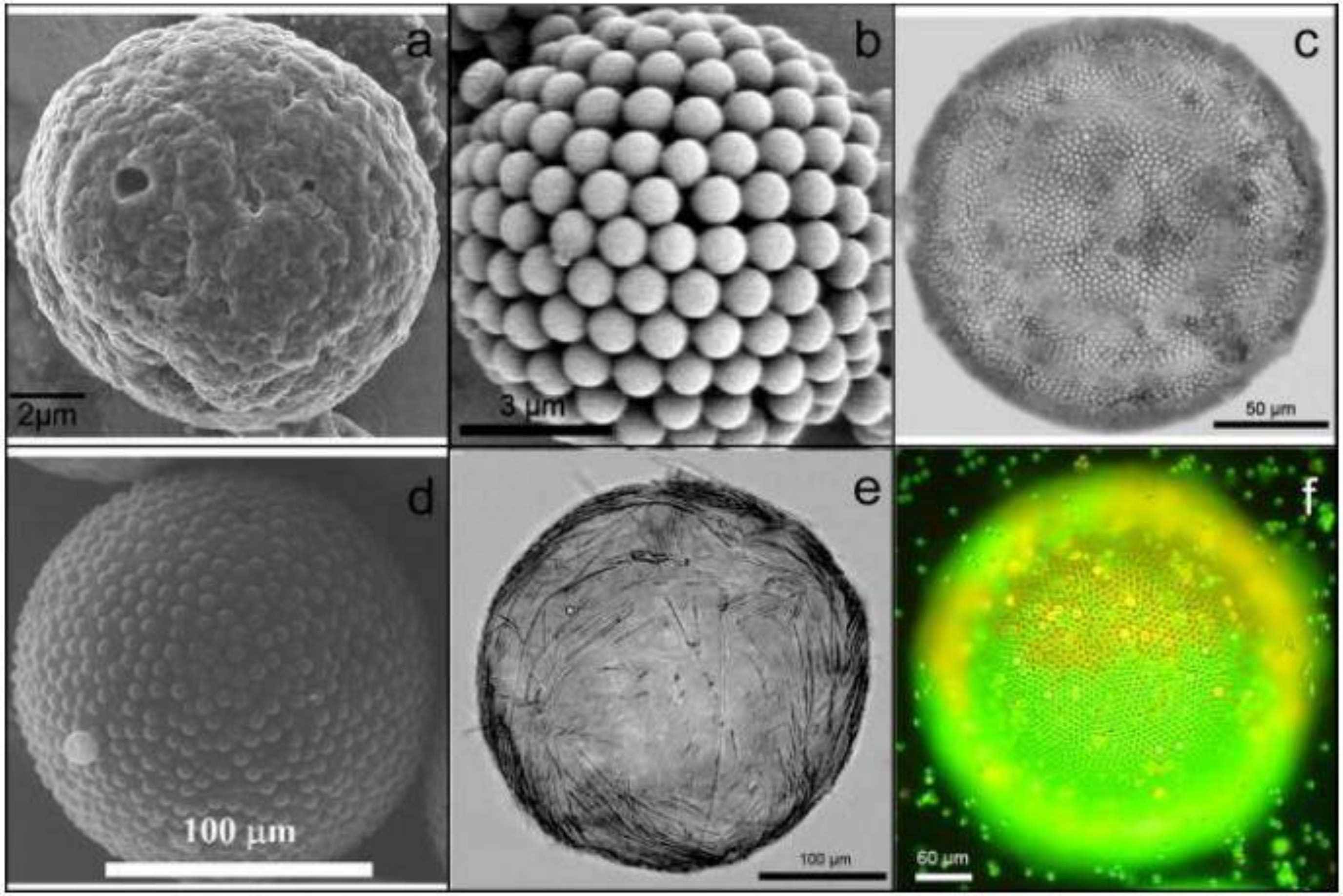
Colloidosomes

Composition and permeability



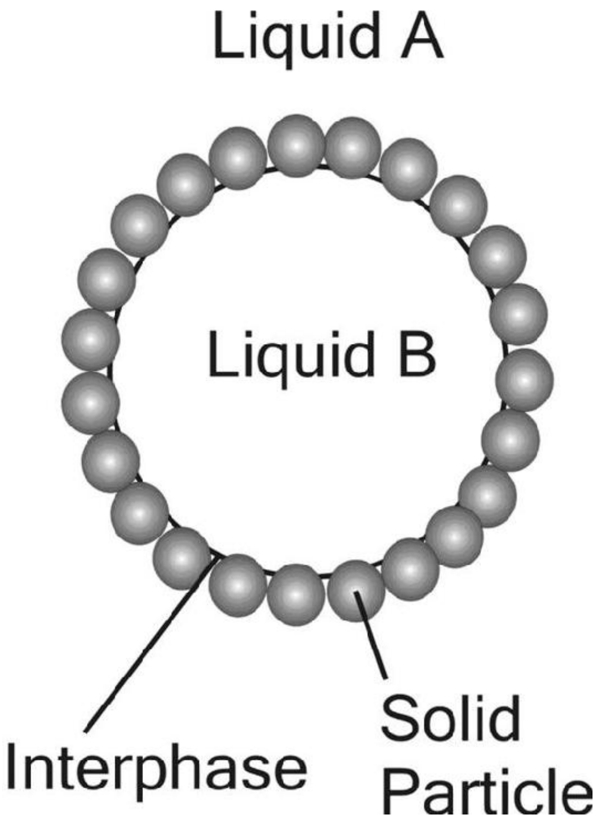
A.D. Dinsmore et. Al., Science, **298**, 1006 (2002); David Weitz group: Harvard Univ.

Pickering (1907) : Emulsions
Dinsmore et al. Science (2002): "Colloidosomes"



Dinsmore et.al.

Capillary binding



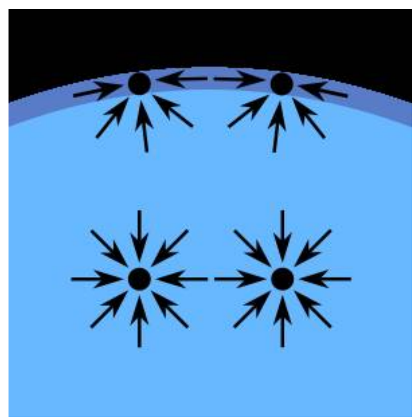
Surface Energy: $E = \gamma A$

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

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.

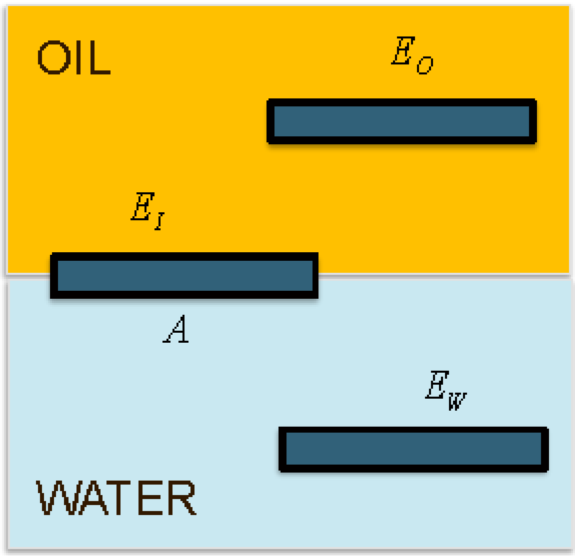
Origin of capillary binding:
Surface tension:

The forces on molecules of a liquid:



Surface tension preventing a paper clip from submerging

Capillary binding of a flat 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 :

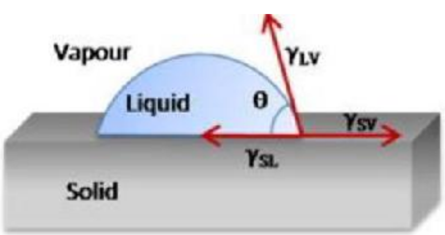
$$E_I - E_O = -A\gamma_{OW}\left(1+\cos\theta\right)$$

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

Wetting angle Young's relation:

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

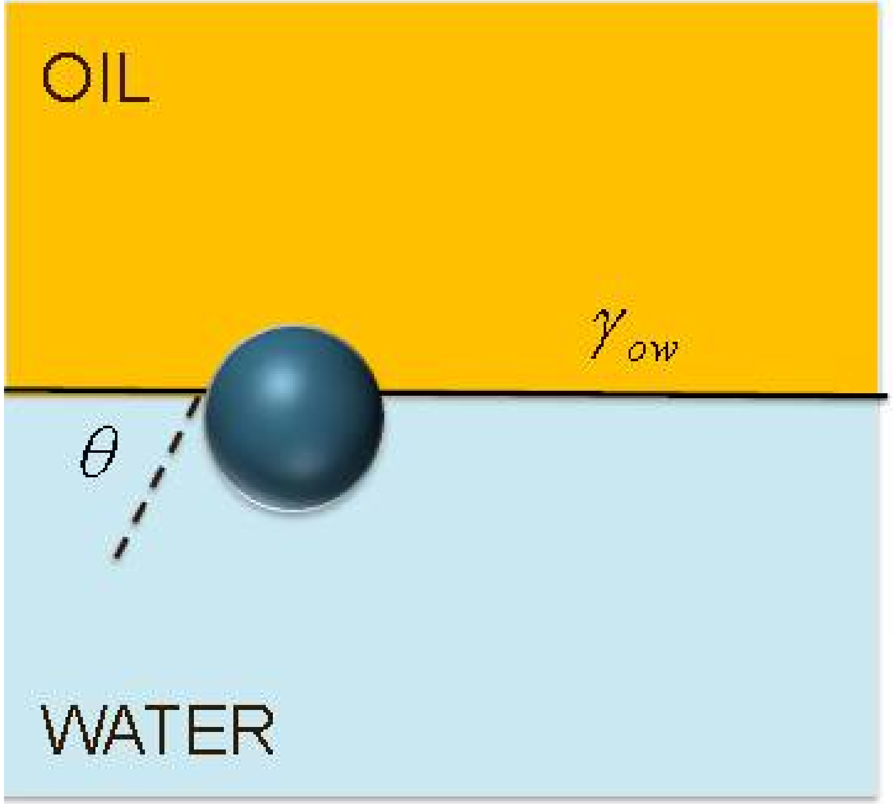
Energetically favorable to adsorb particles at the interface.



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

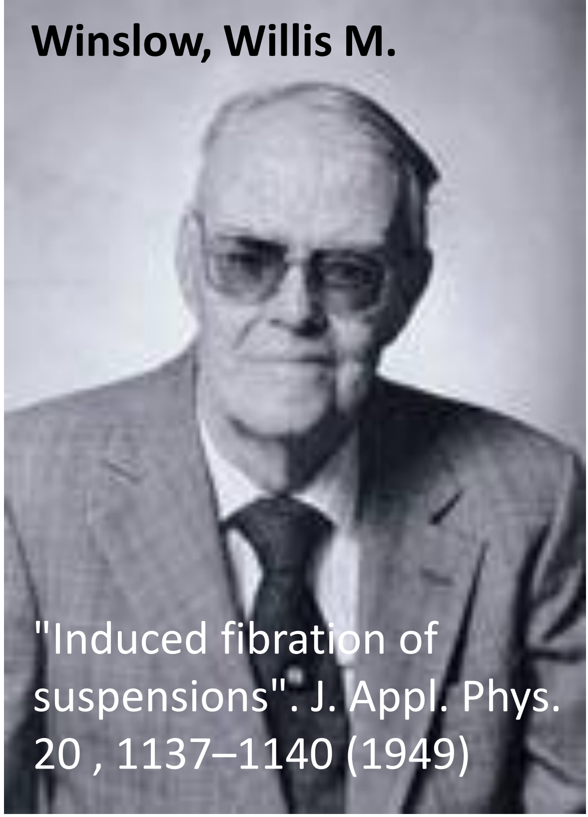
Kan Du †, Elizabeth Glogowski ‡§, Todd Emrick ‡, Thomas P. Russell *‡ and Anthony D. Dinsmore *†
† Physics Department
‡ Polymer Science and Engineering Department
University of Massachusetts, Amherst, Massachusetts 01003
§ Department of Chemistry, University of Illinois at Urbana−Champaign, Urbana, Illinois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

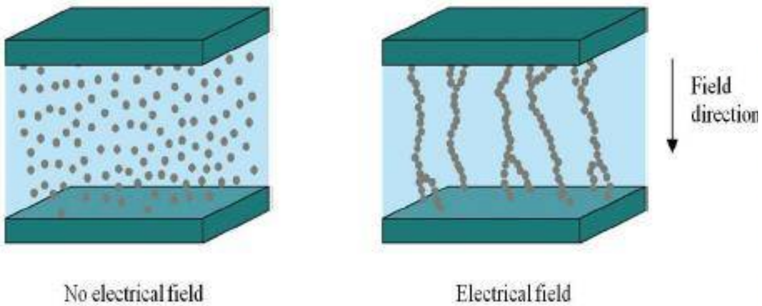
Electro-rheological fluids



Winslow, Willis M.

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

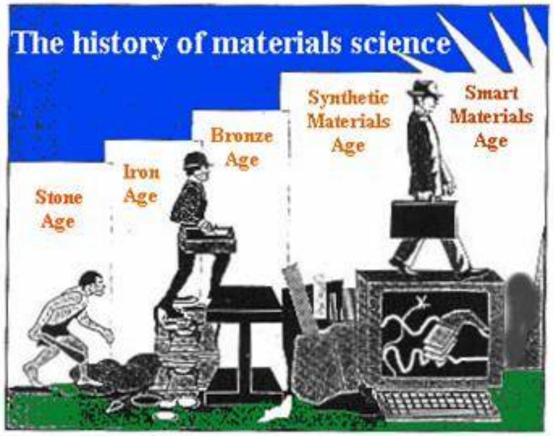
Winslow effect:

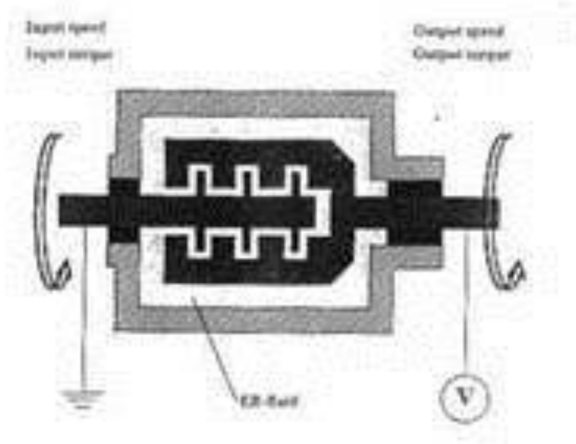


Viscosity can increase by a factor 100 000 in response to an electric field!

- 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)

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

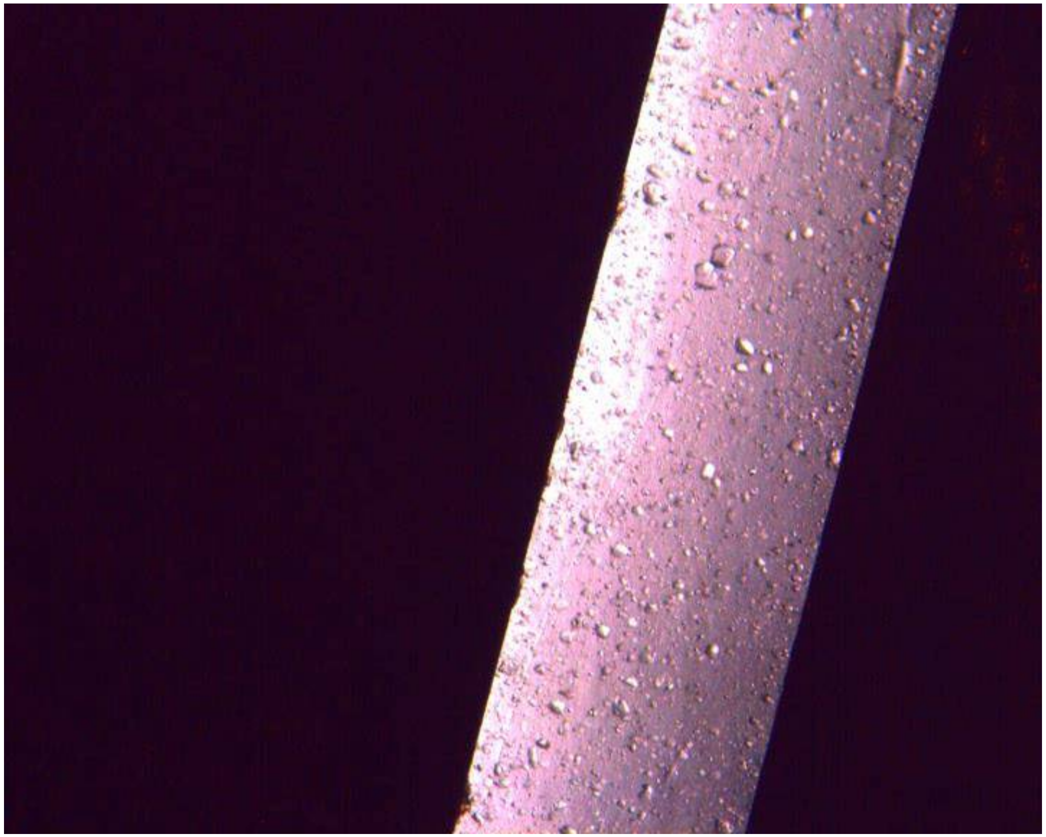




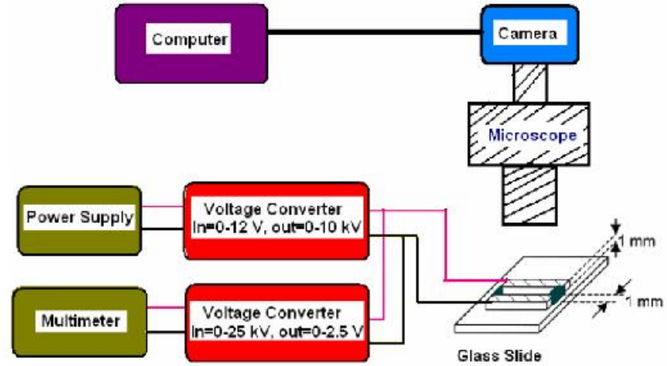
Clay particles suspended in oil:

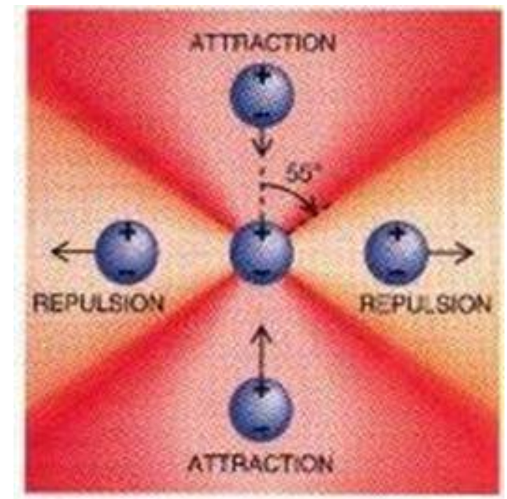
Video microscopy (real time):

~500 V



1 mm

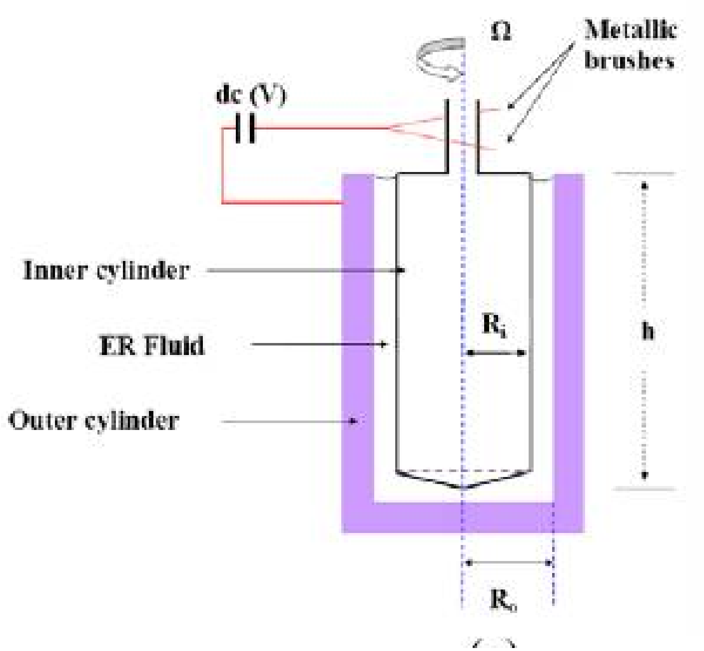




Electrorheology: Smart Materials

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:



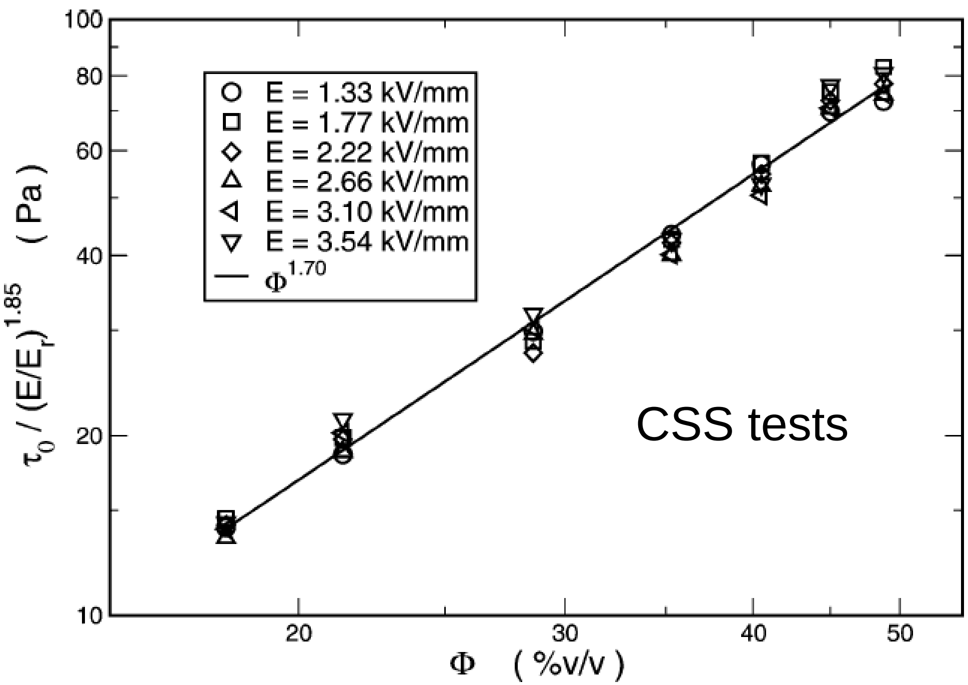
Langmuir 24, 1814 (2008)

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.

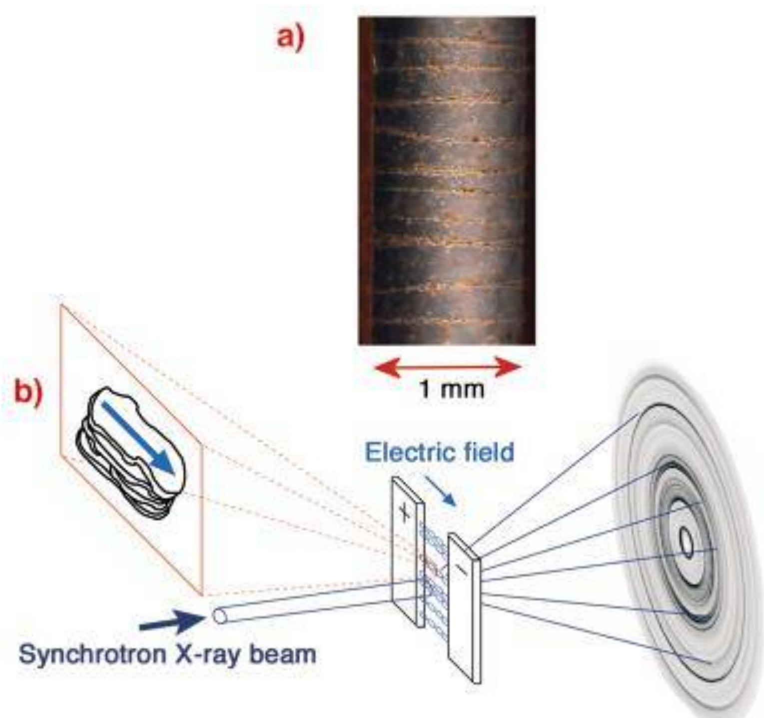
Log-log plot of the static yield stress, normalized by $E^{1.86}$, vs. the volume fraction at different strengths of the applied electric field. A power law β ≈ 1.70 fits to the whole dataset..

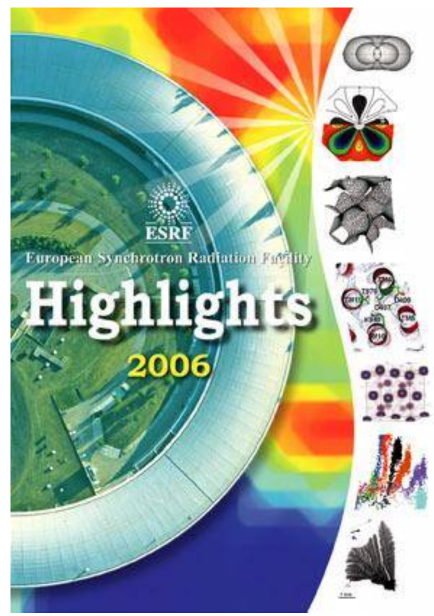
ER Suspensions of Laponite in Oil — *Langmuir, Vol. 24, No. 5, 2008* 1821

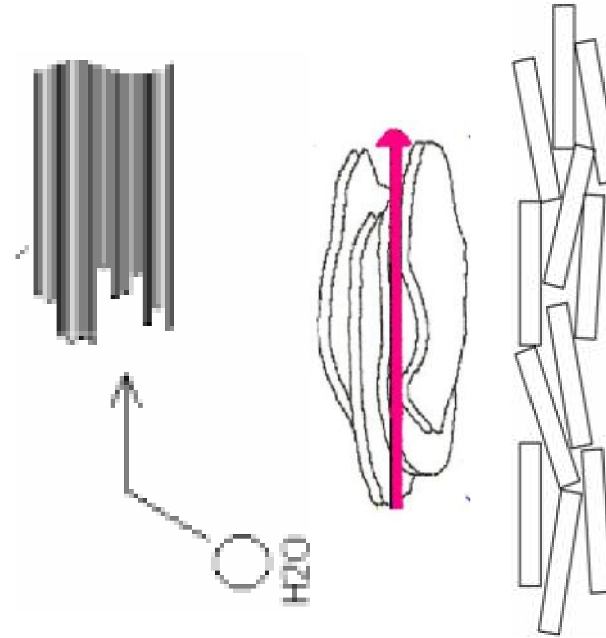
Table 1. Comparison of Static Yield Stress Values for Various ER Fluids Including That Addressed in the Present Paper, under an Applied Electric Field of About 1.0 kV/mm

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

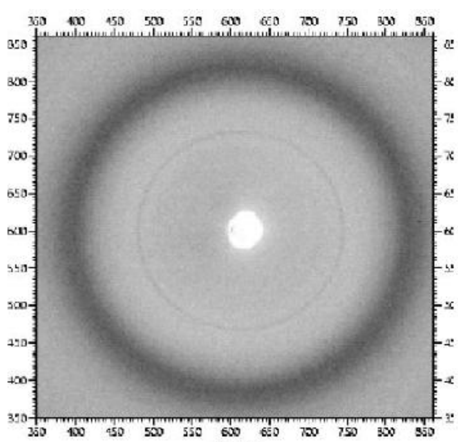
Experiments at ESRF, Grenoble:
In ESRF Scientific Highlights 2006



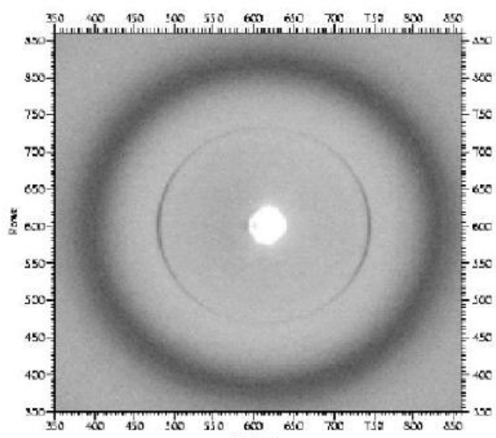


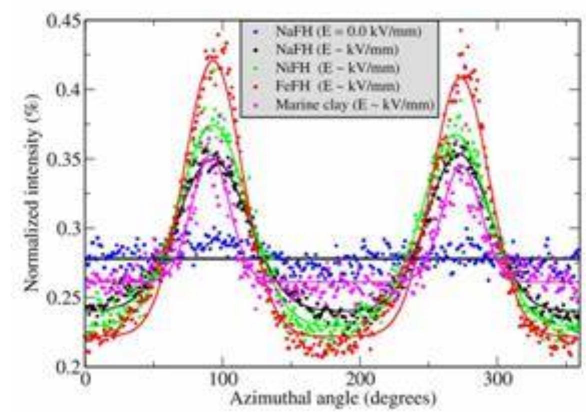


Before: 0 V/mm

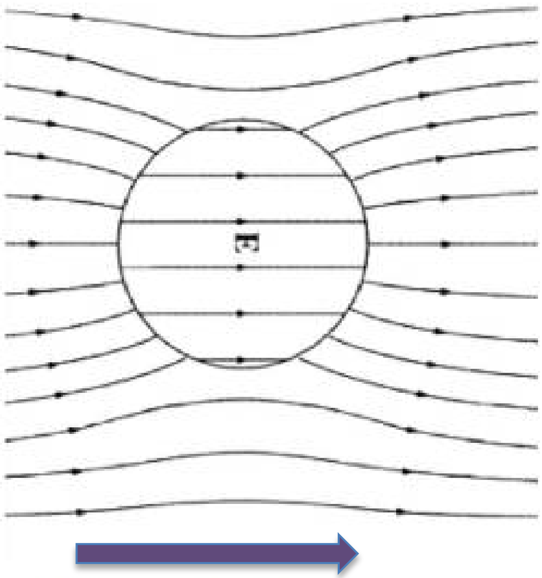


After: 500 V/mm

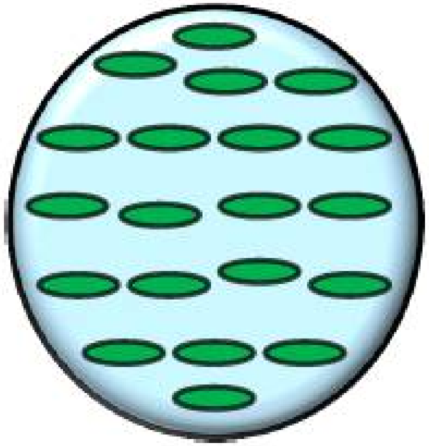




Angular distribution function
$= S_2 = \frac{1}{2}\langle 3\cos^2\theta - 1 \rangle$



Electric field



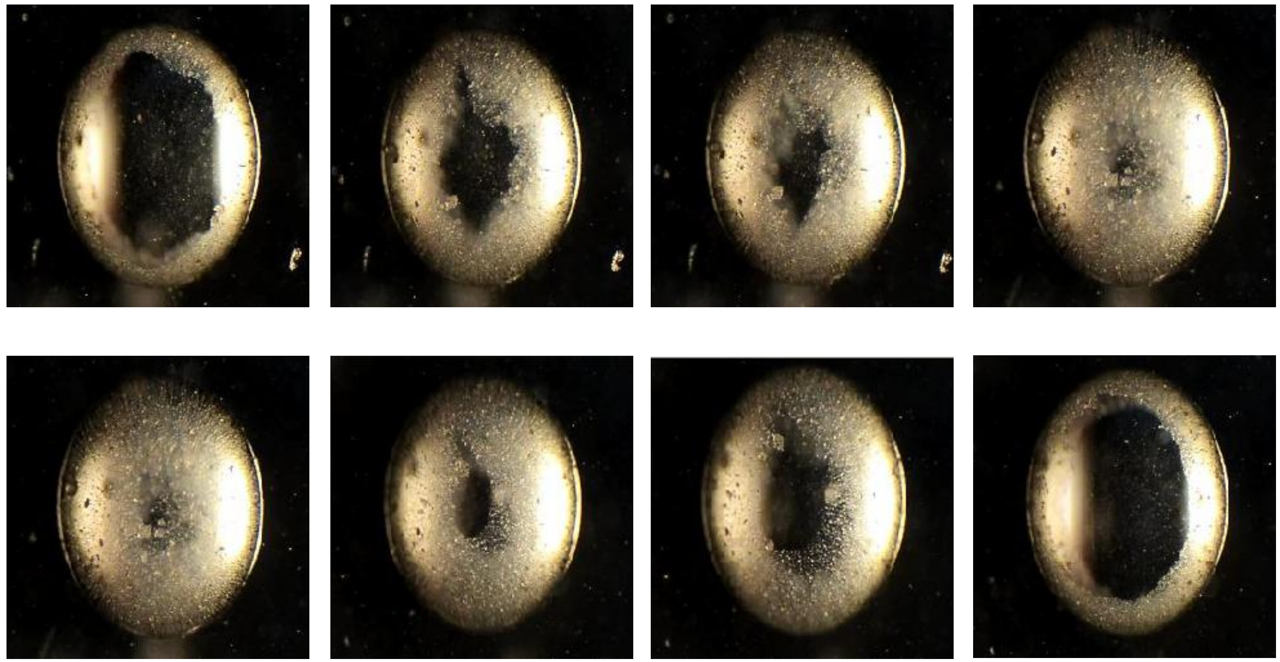
Chain formation inside a drop?

Electrorheological droplets for microfluidics
Electrorheological emulsions

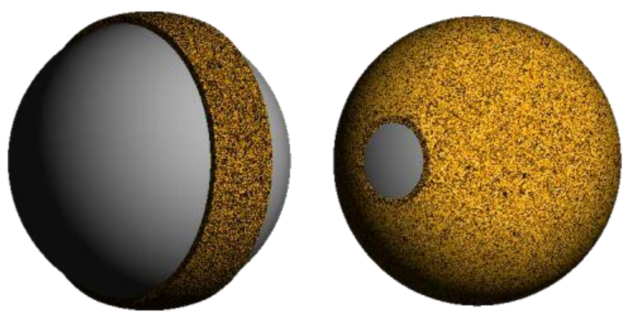
Is it possible to make electrorheological drops?

200 → 500 V/mm

200 ← 500 V/mm



Electro-hydrodynamic flow



Dipole-dipole interactions

Active pupil-like colloidal shell (opening - closing)

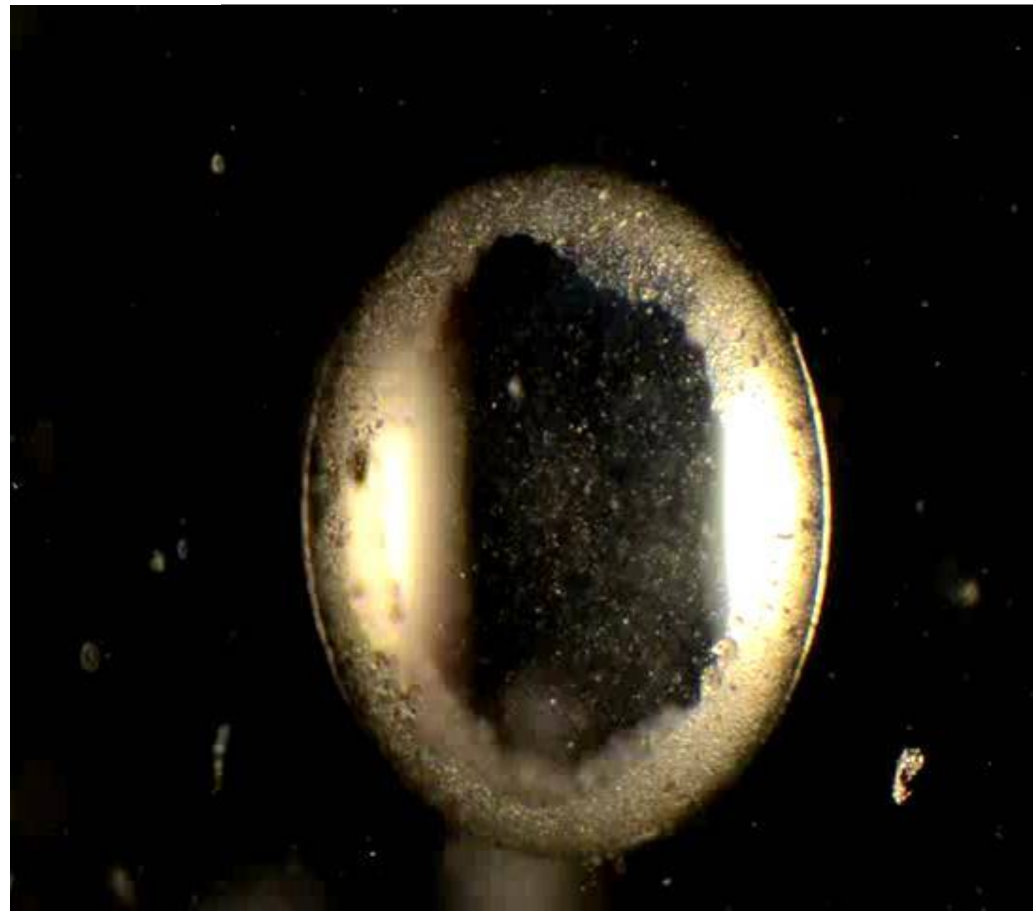
nature COMMUNICATIONS

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

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

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

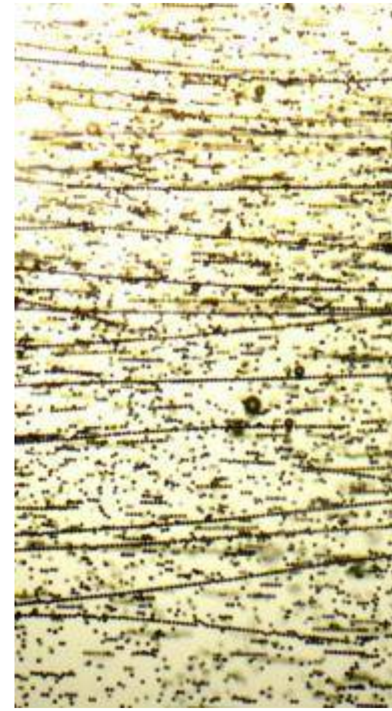
Very high E-field

Clay particles

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

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

Hundreds V/mm



Ag coated beads

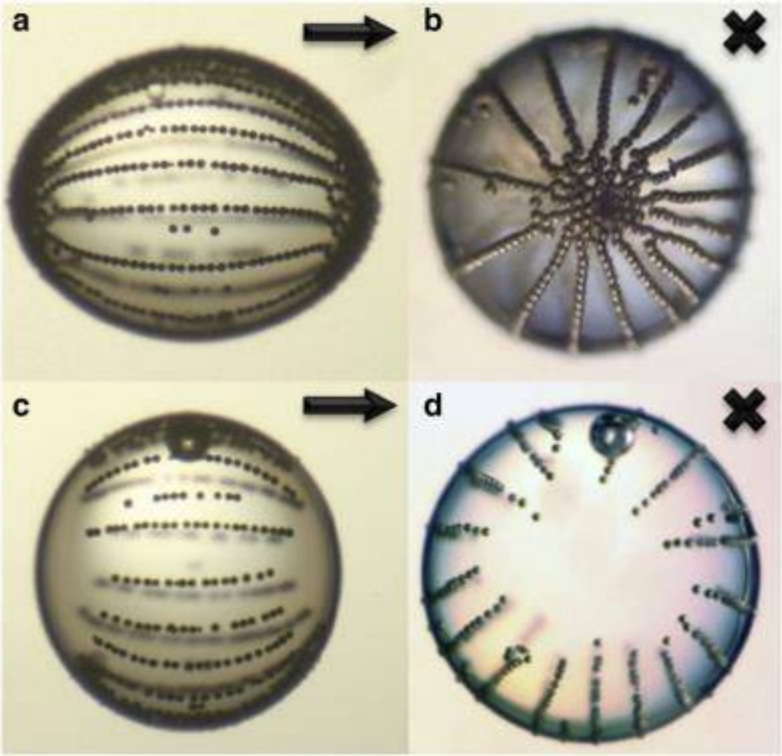
$\varepsilon_{oil} \ll \varepsilon_{particles}$

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

Tens V/mm

Particle dipole-dipole interactions

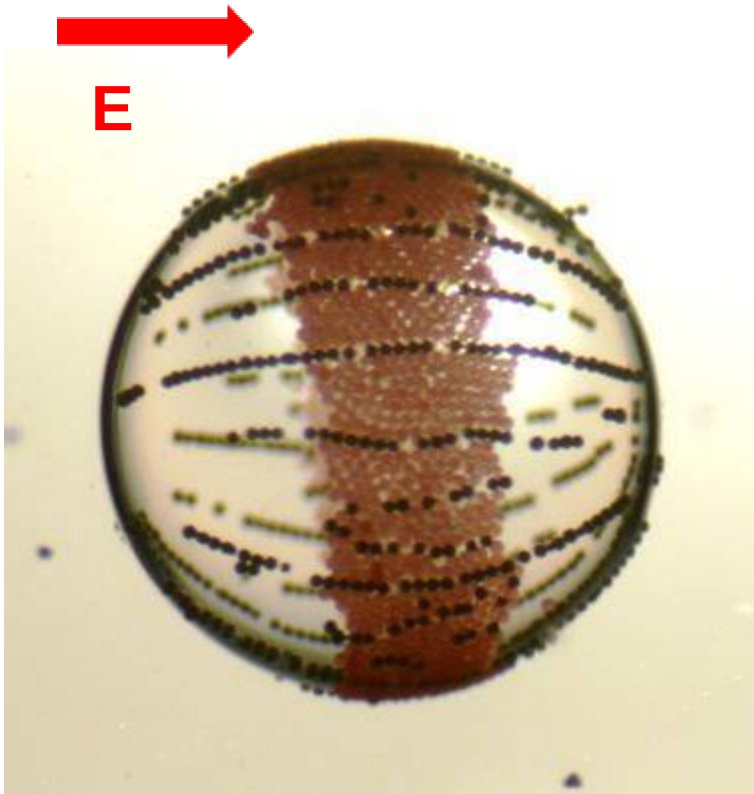
Drop “behind bars”

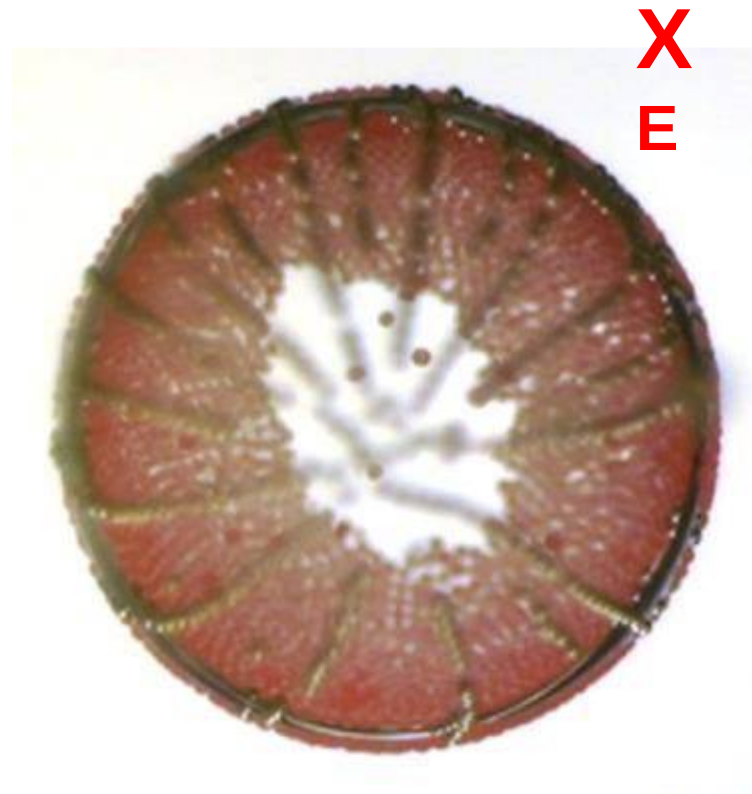


Matallic conducting beads on the surface of a silicone drop with a radius of about 1 mm embedded in castor oil

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

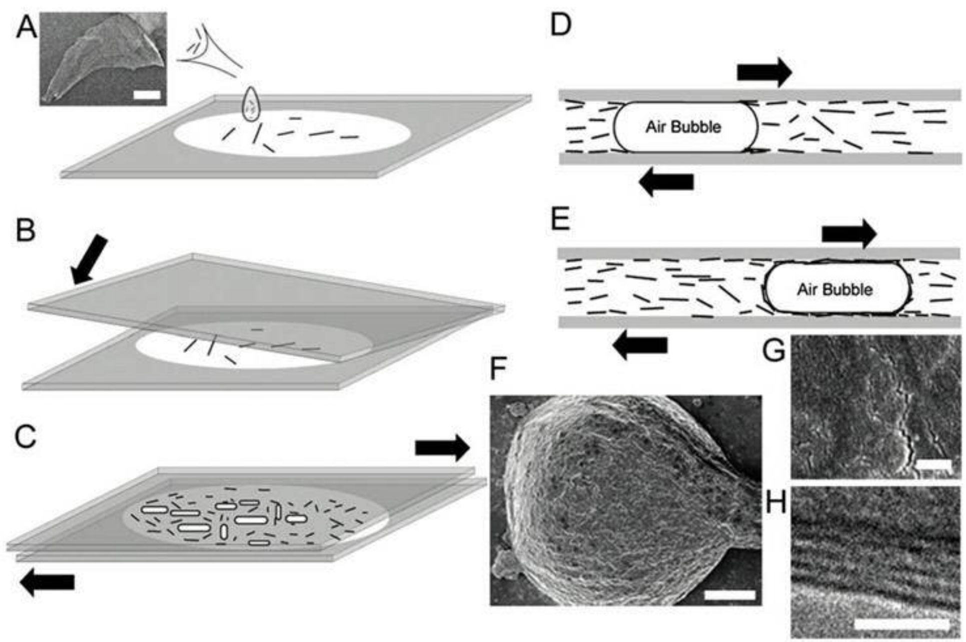
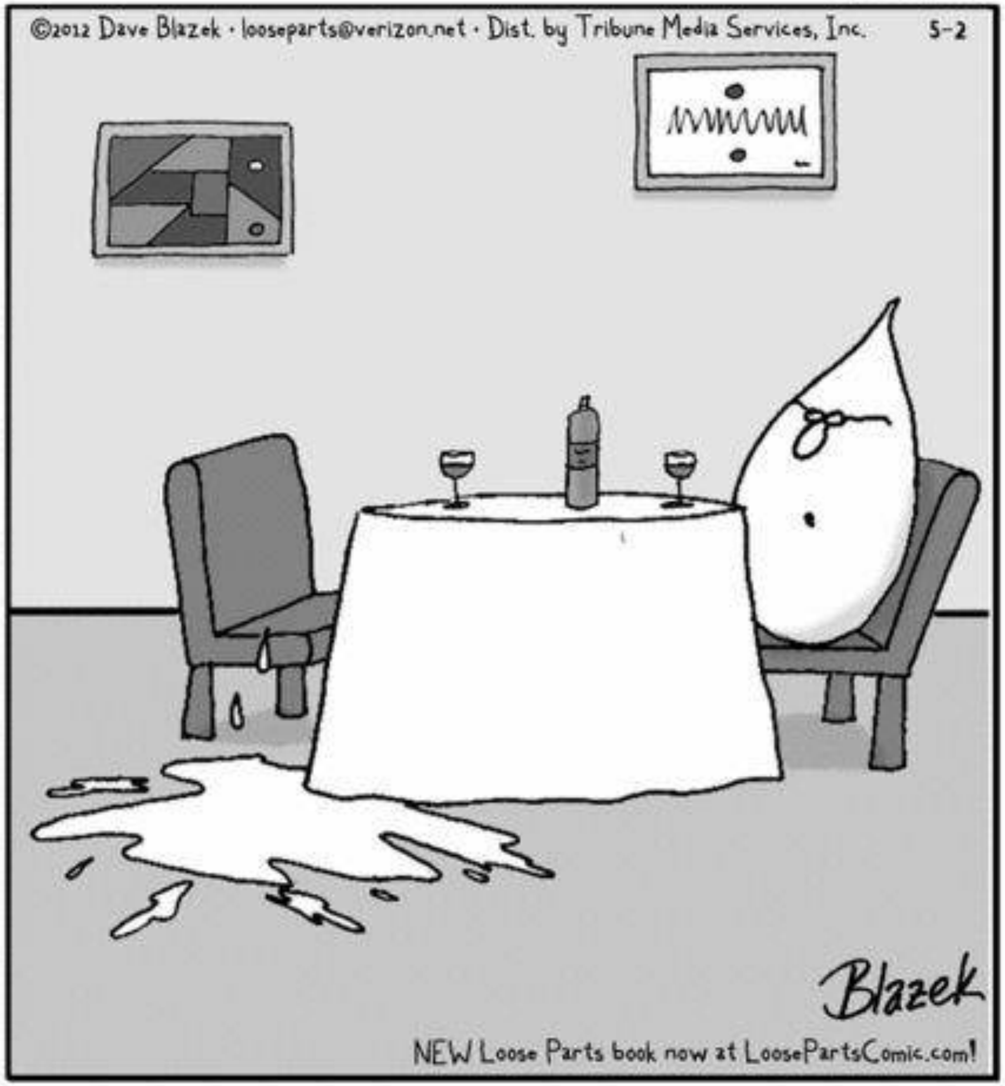


Fig. 1 Formation of clay armored bubbles. (A, inset) TEM image demonstrating the plate-like structure of the clay montmorillonite. (A) An aqueous suspension of clay is placed on a glass slide. (B) A second glass slide is engaged on the first glass slide, trapping pockets of gas in the process. (C) The 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.

LOOSE PARTS

DAVE BLAZEK



"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 DOI: 10.1038/ncomms4945 OPEN

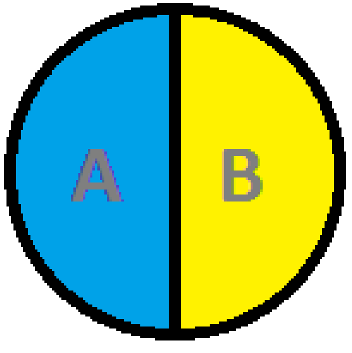
Electroformation of Janus and patchy capsules

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.

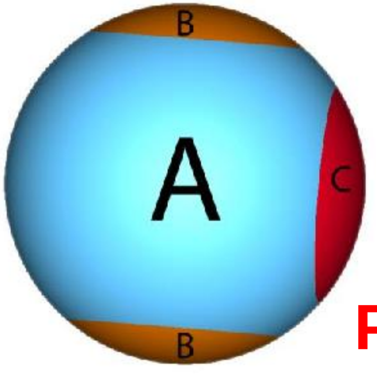
Usually depicted with **two faces**, looking to the future and to the past



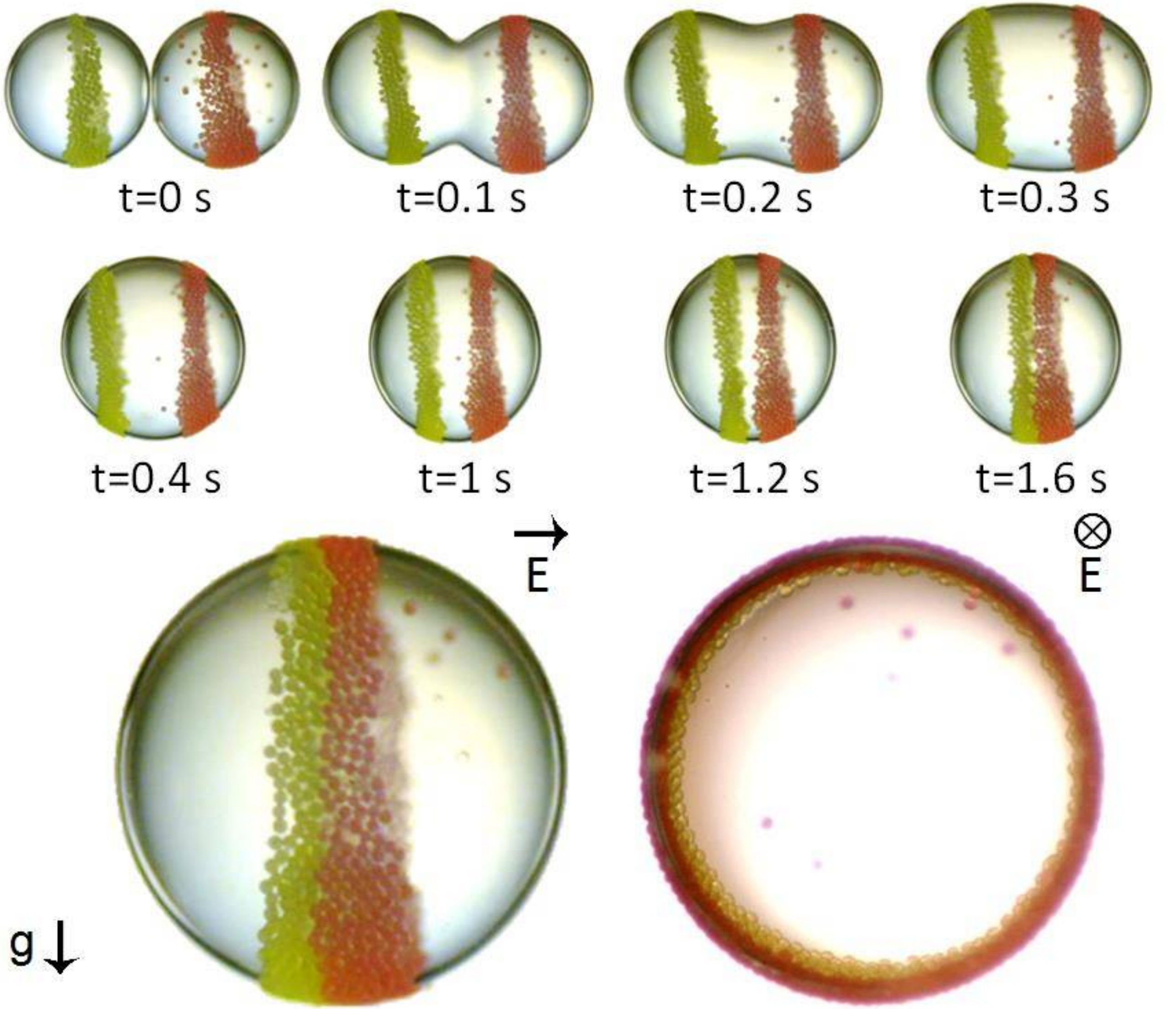
Pierre-Gilles de Gennes Nobel Prize lecture, 1991

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



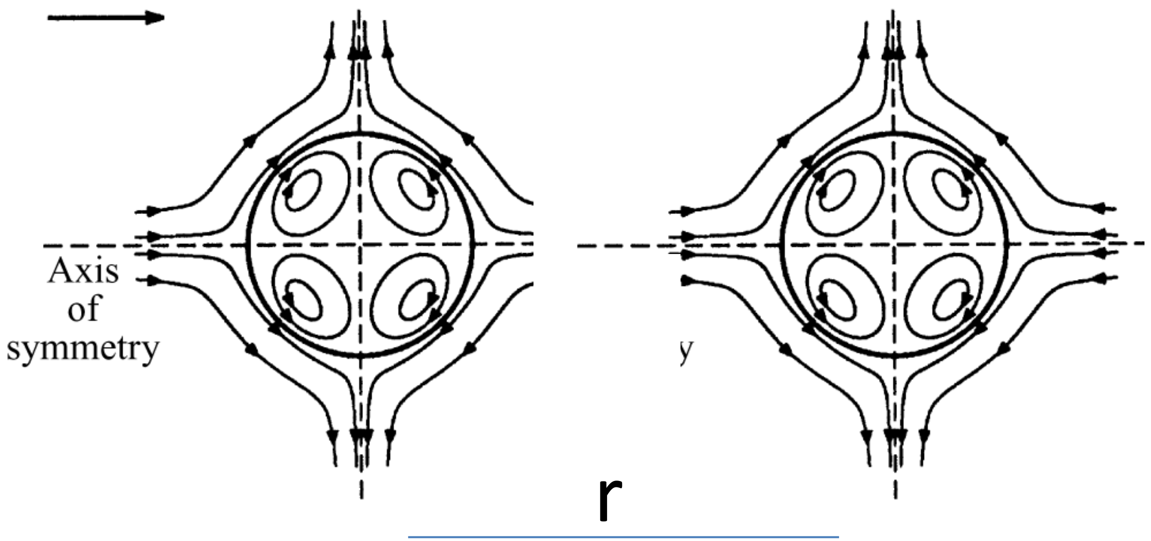
Final state viewed perpendicular and parallel to the E-Field

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]



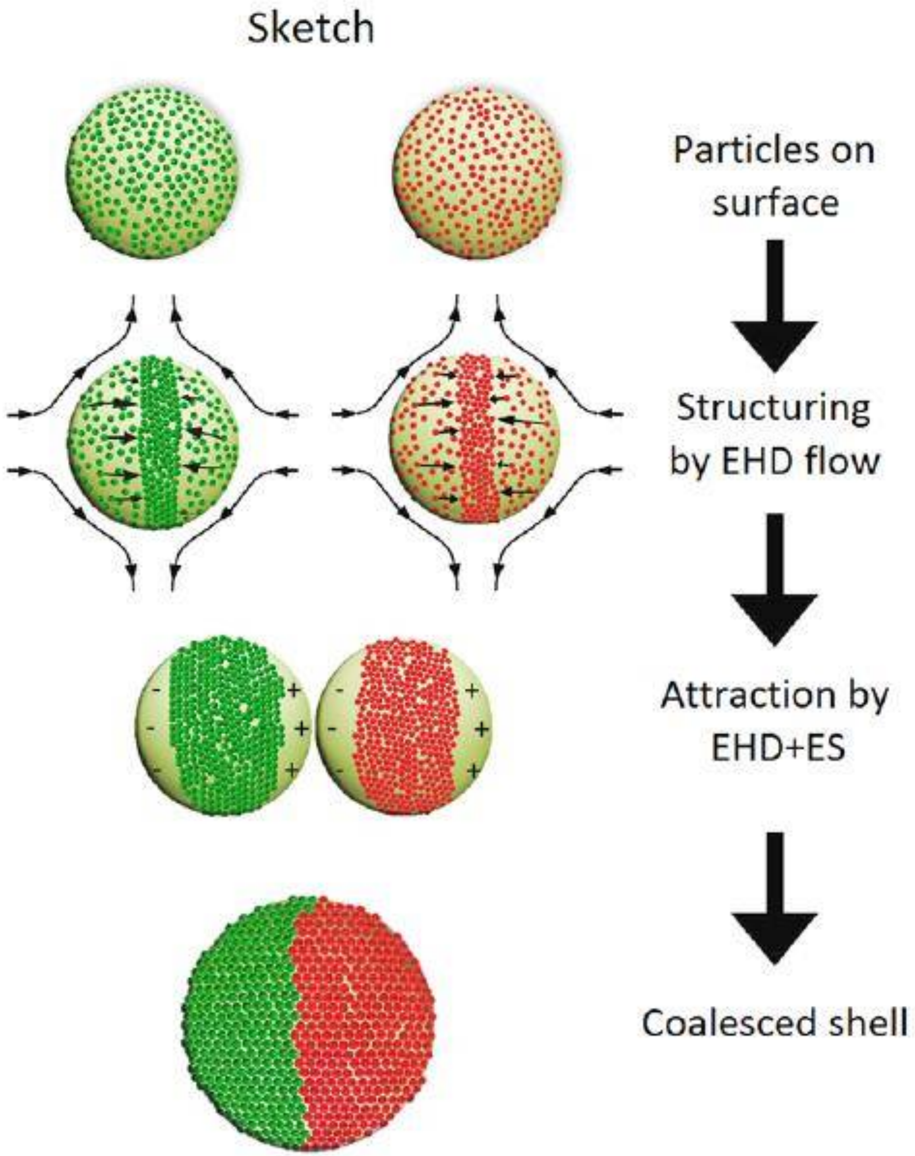
$$V_{hydro} \propto \frac{1}{r}$$

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

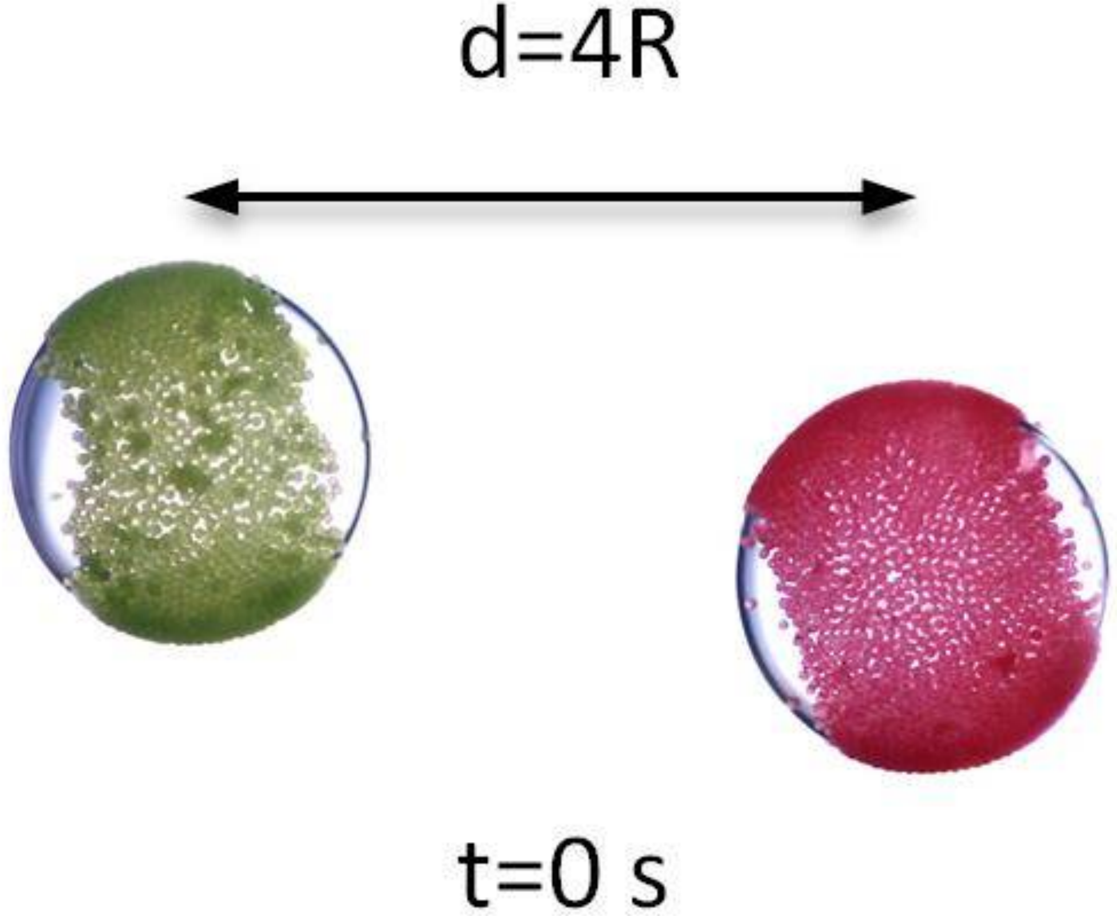
$\hat{\tau} > \tau$ Attractive hydrodynamic interaction

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

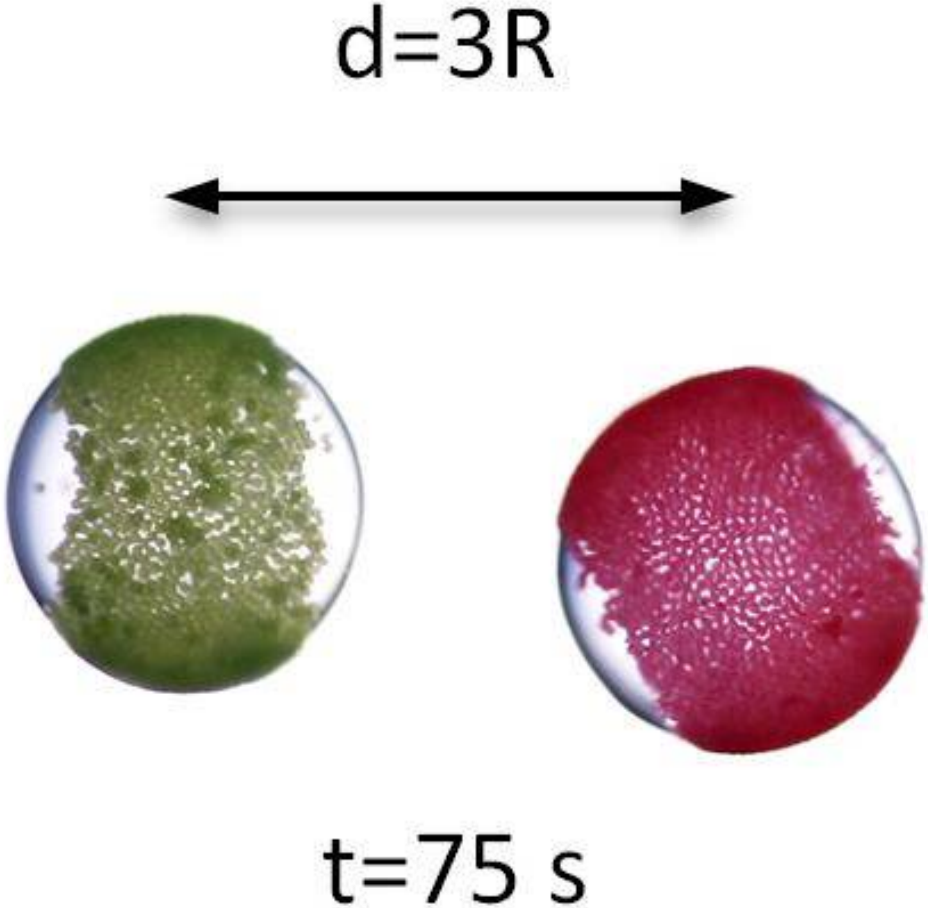
Hydrodynamic interactions are stronger than dipole-dipole interactions



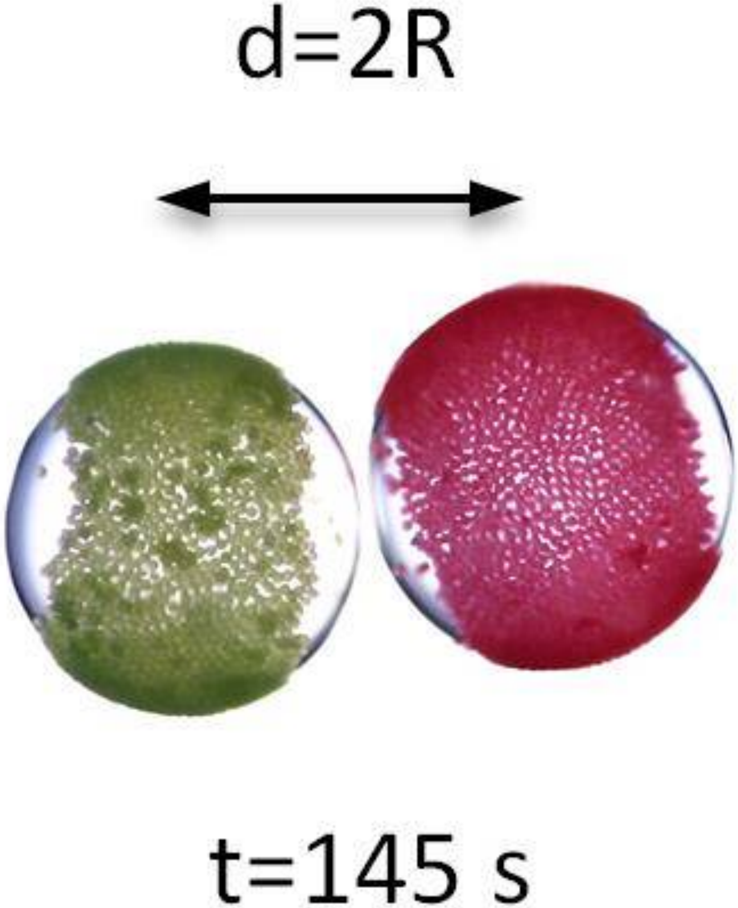
Fabrication of Janus shell: Experiments at NTNU Trondheim

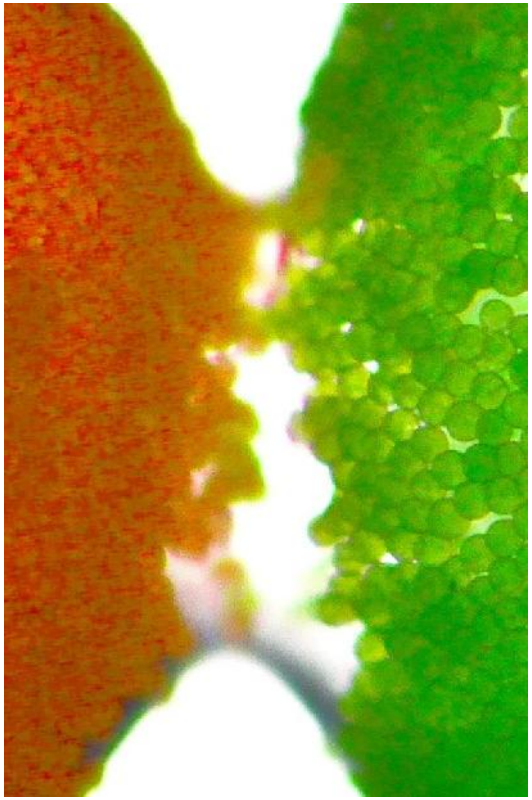


Fabrication of Janus shell: Experiments at NTNU Trondheim



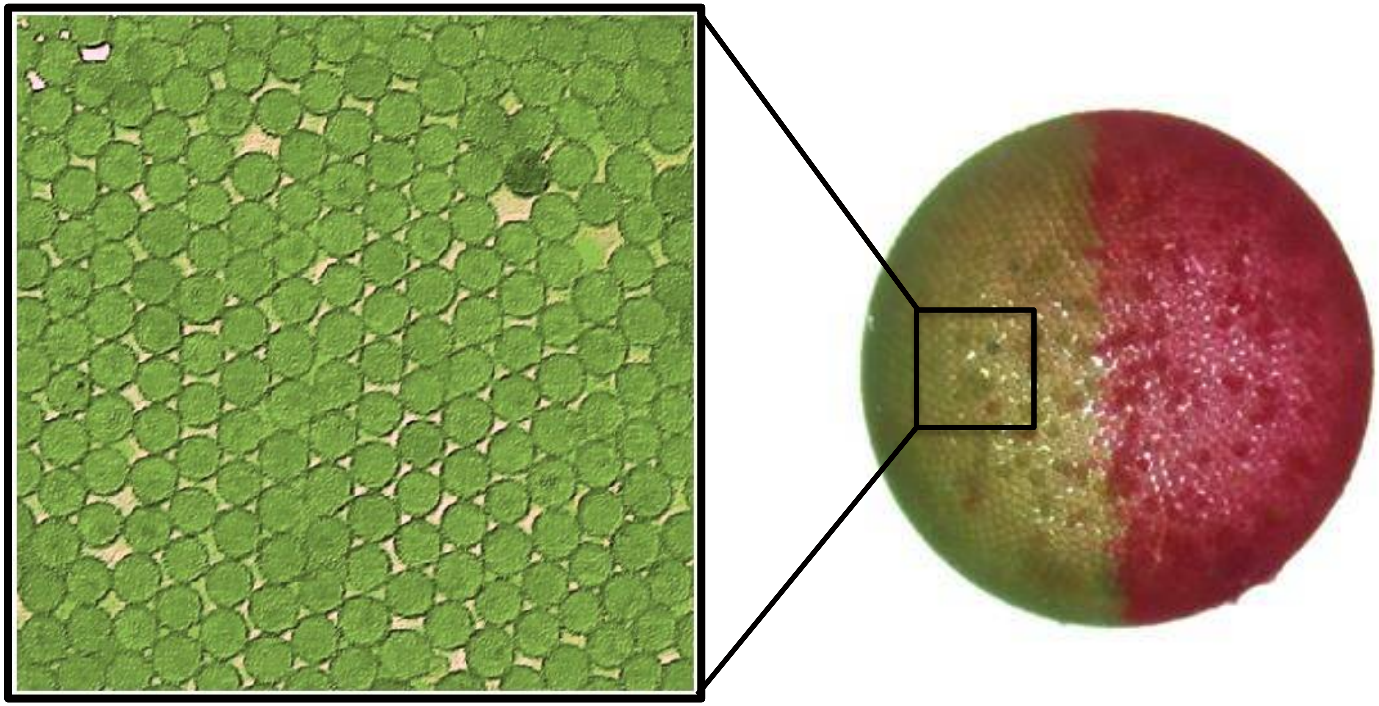
Fabrication of Janus shell: Experiments at NTNU Trondheim



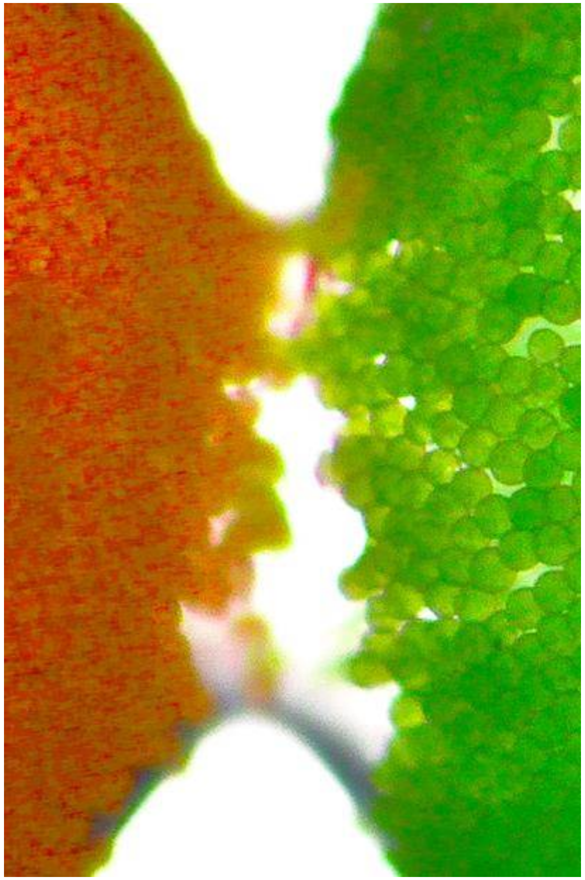


Fabrication of Janus shell: Experiments at NTNU Trondheim

Janus shell



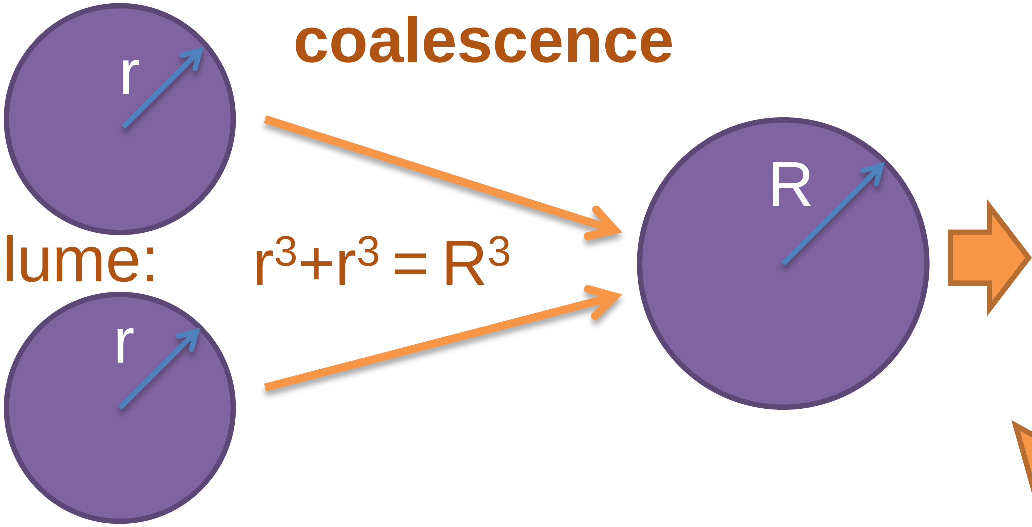
Hexagonal packing: Experiments at NTNU Trondheim



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:



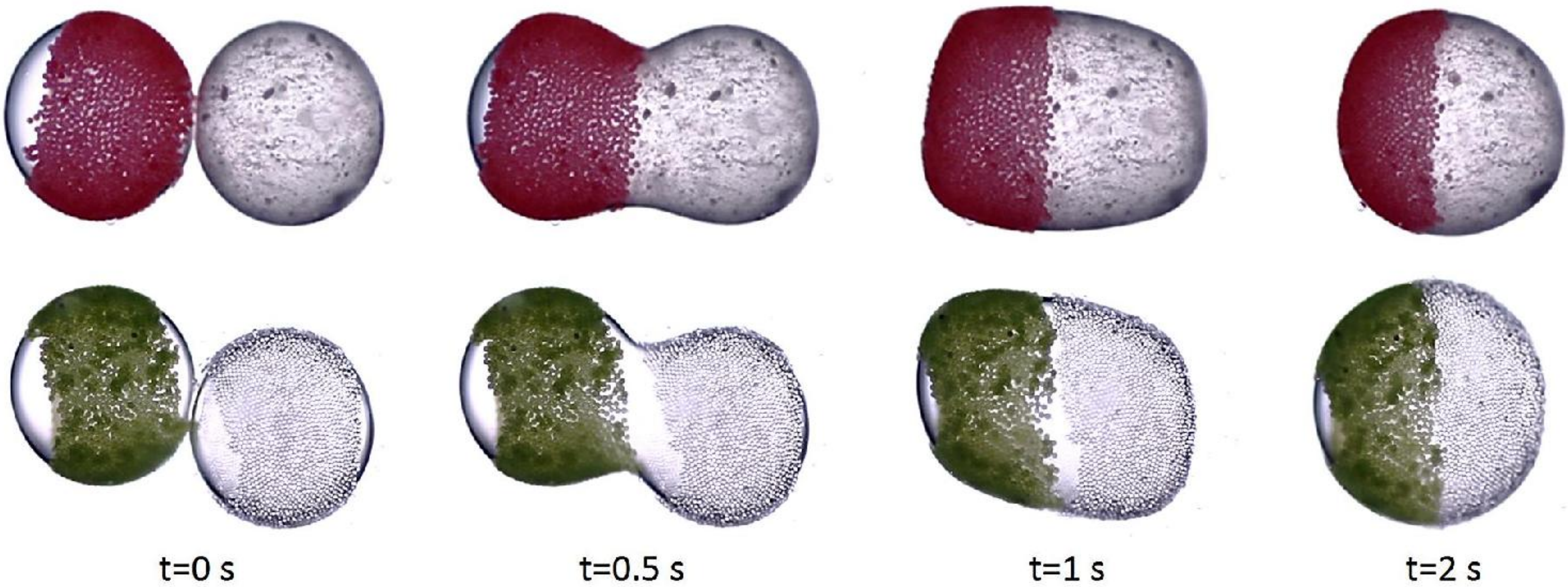
Volume: $r^3+r^3 = R^3$

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

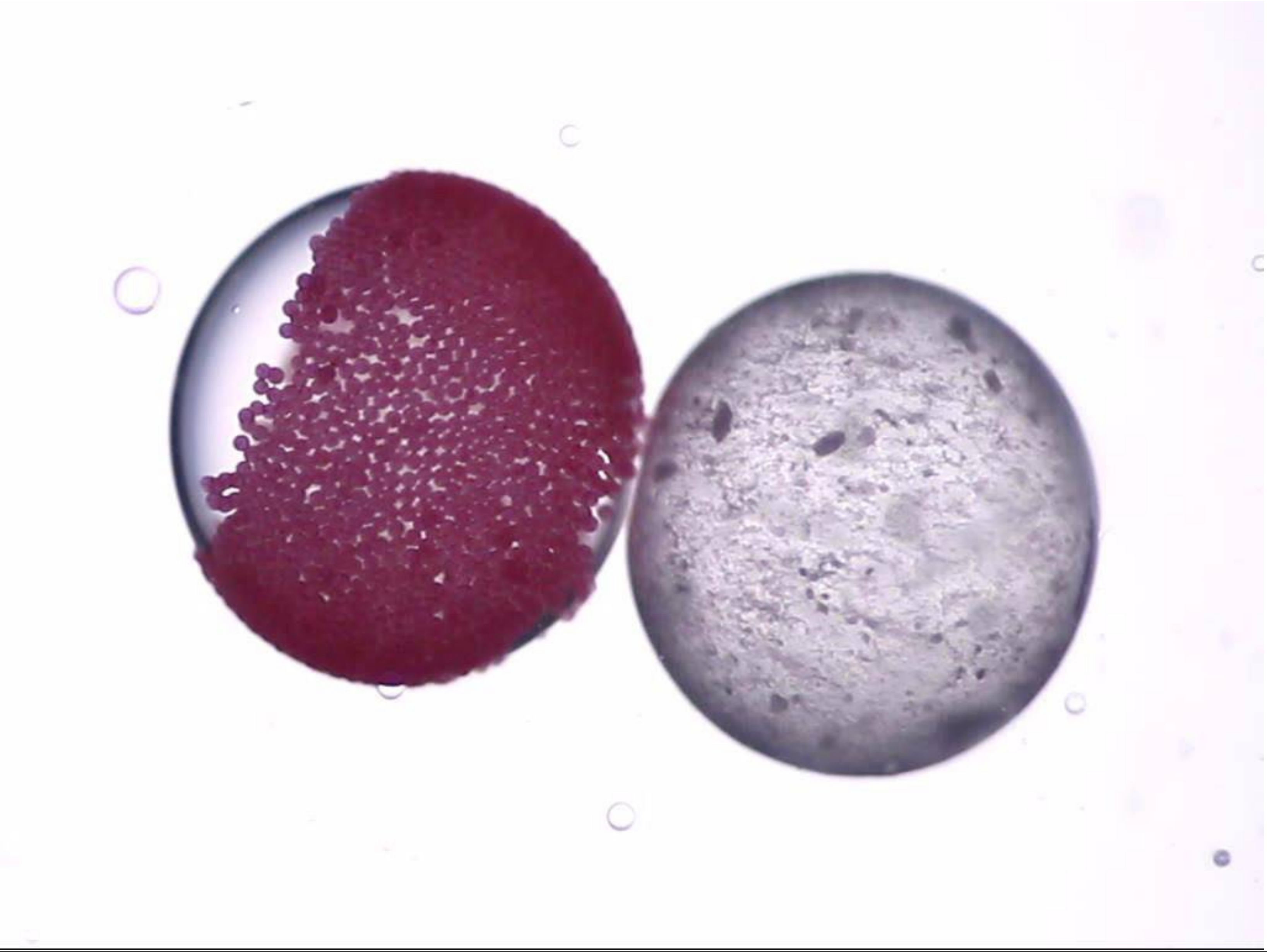
Area: $R^2 = 2^{-1/3}2r^2 = 2^{-1/3}(r^2+r^2\ )$

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

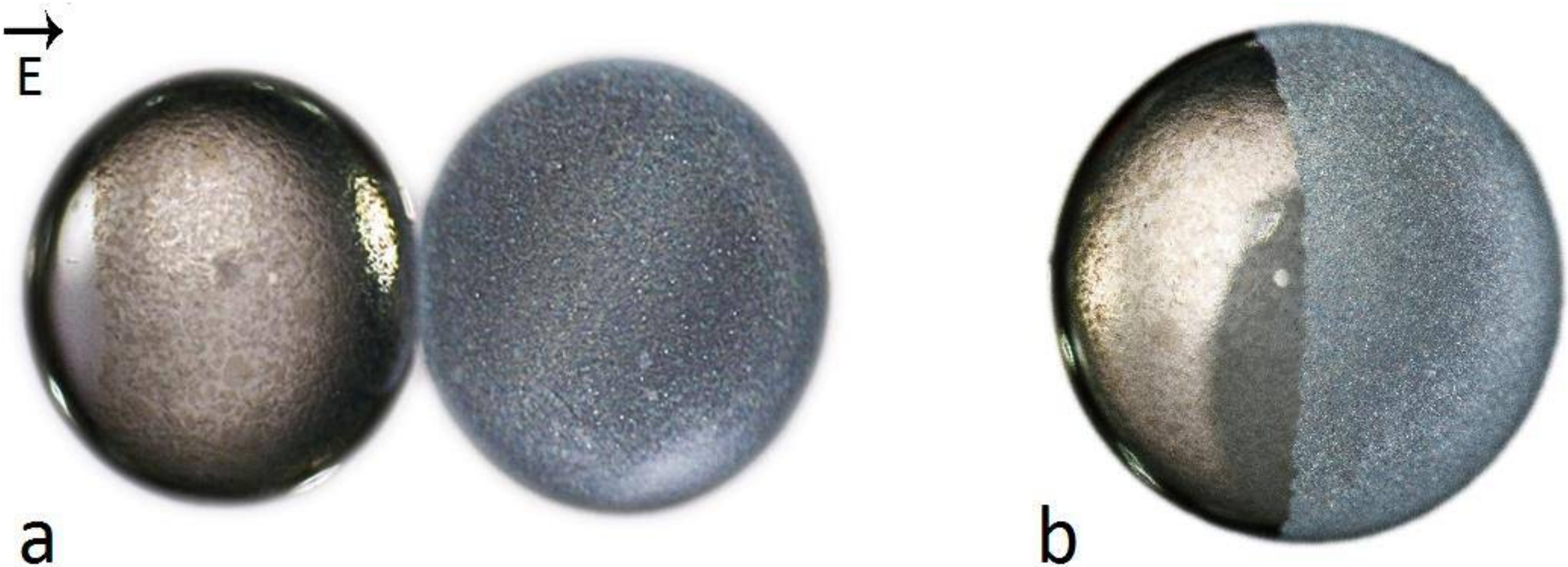
$\Rightarrow$ Final drop can be fully covered even if the original drops are not



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



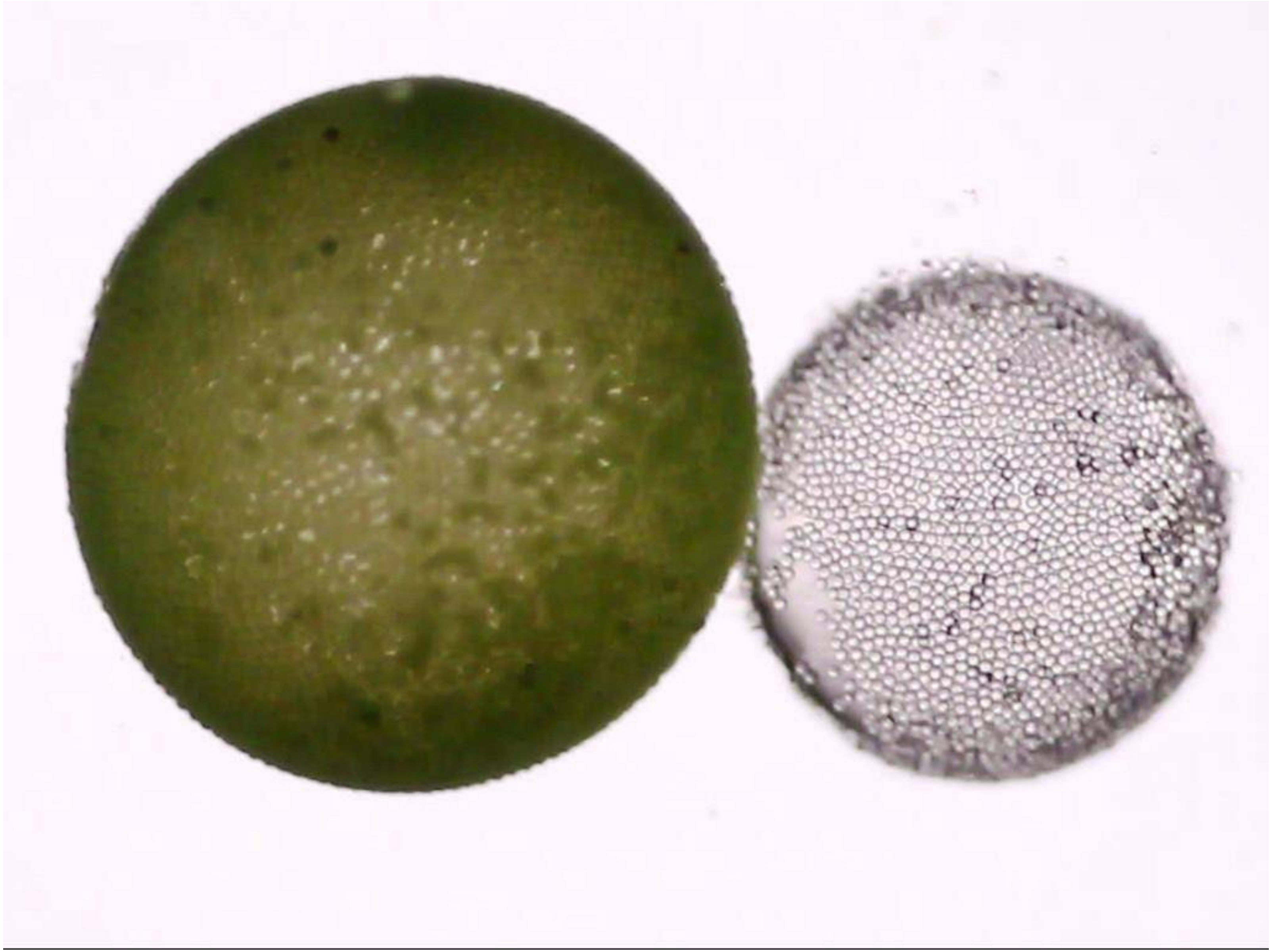
Janus shells with clay and PE particles:
Experiments at NTNU Trondheim



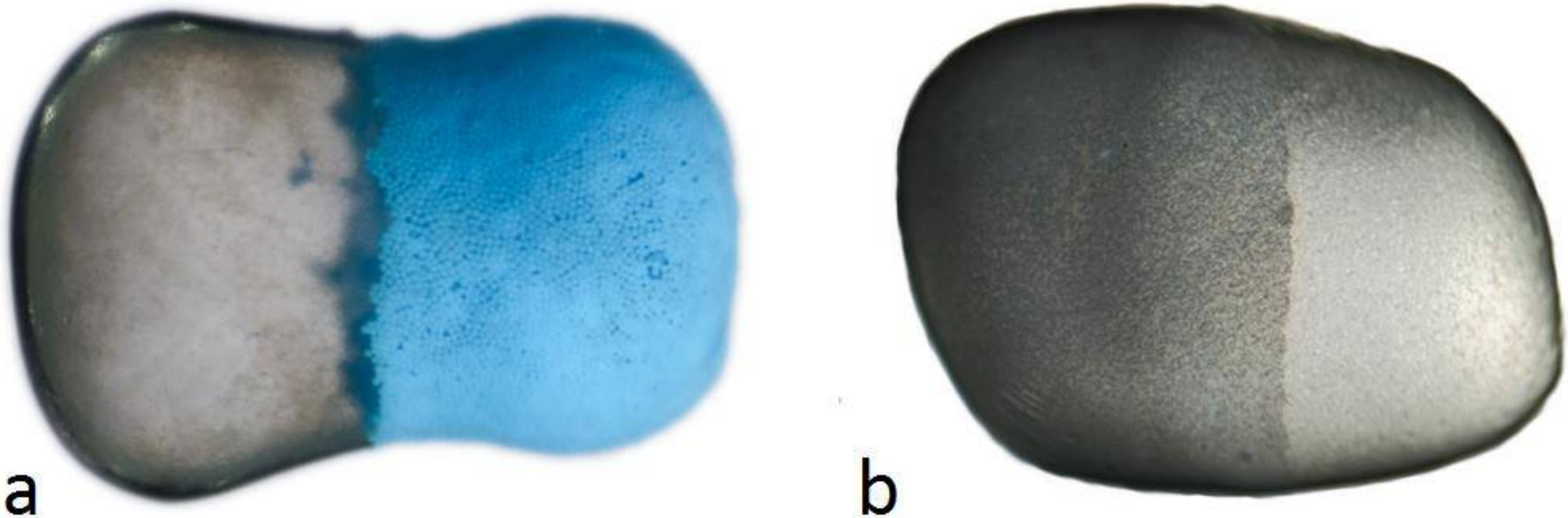
Spherical Janus shell: 1 μm and 500 nm particles:
Experiments at NTNU Trondheim

Arrested shells – symmetric:
Experiments at NTNU Trondheim

Arrested shells – asymmetric:
Experiments at NTNU Trondheim



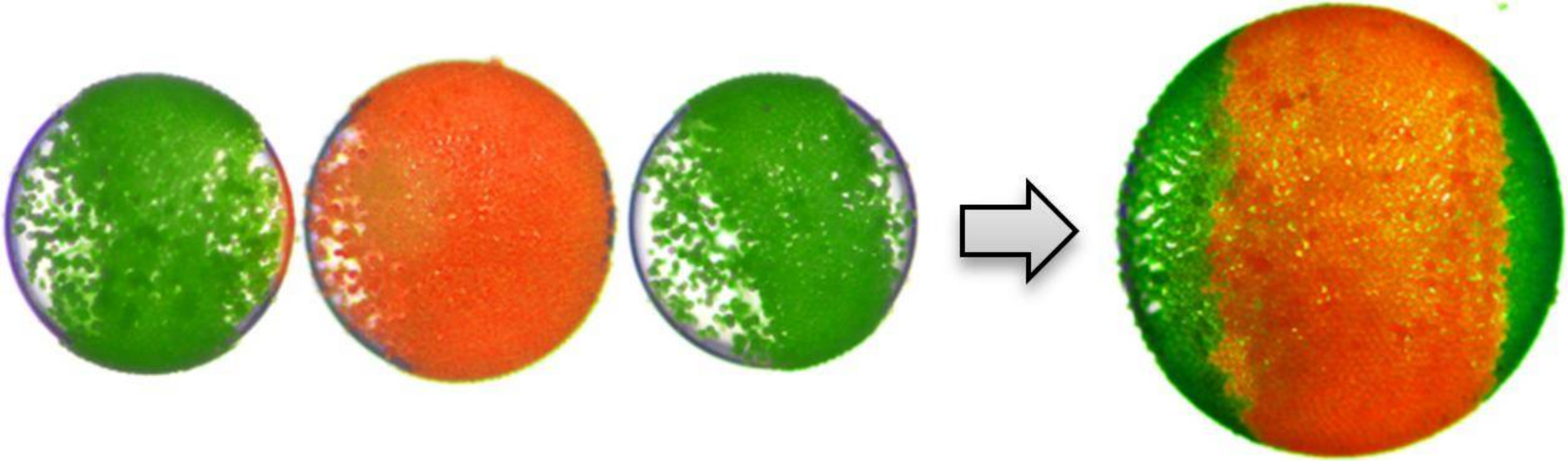
Arrested shells – asymmetric:
Experiments at NTNU Trondheim



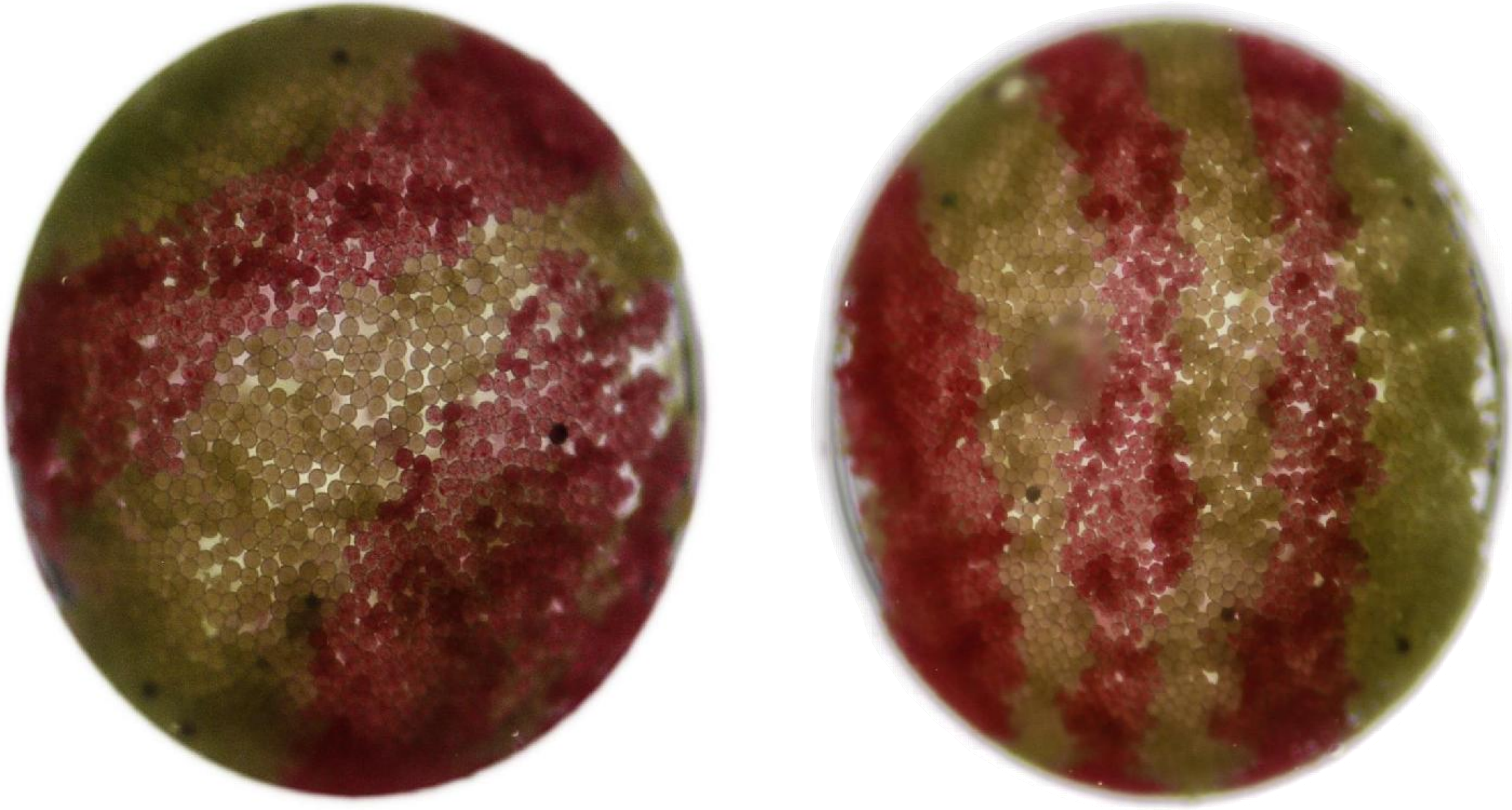
glass (500 nm) and blue PE (20 µm) particles

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

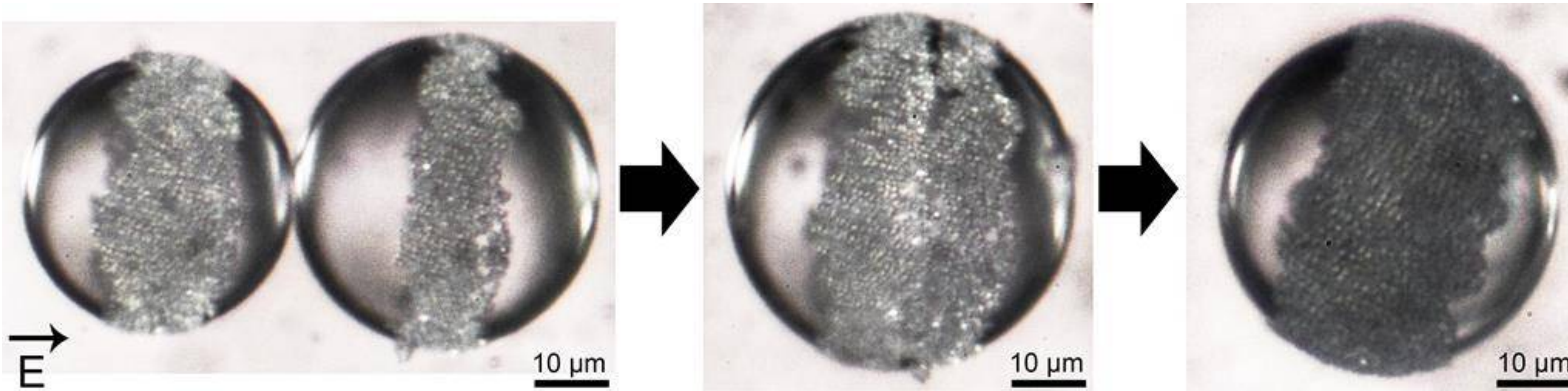
Arrested shells : Small particles: Experiments at NTNU Trondheim



Patchy shells: Experiments at NTNU Trondheim

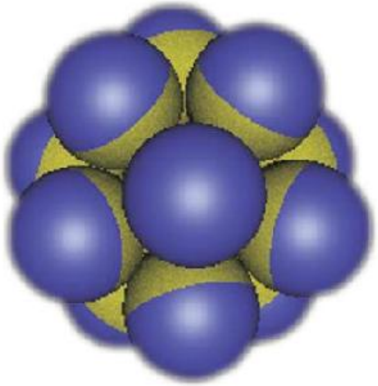


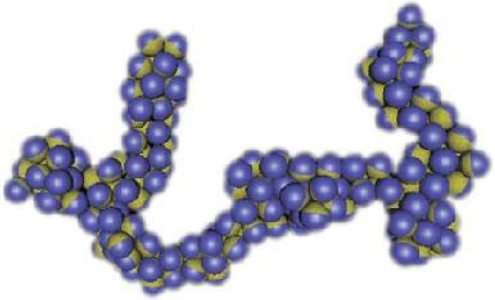
Patchy shells: Experiments at NTNU Trondheim



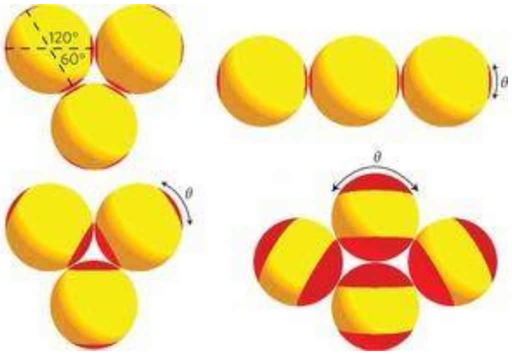
Smaller droplets?: Experiments at NTNU Trondheim

Janus shells

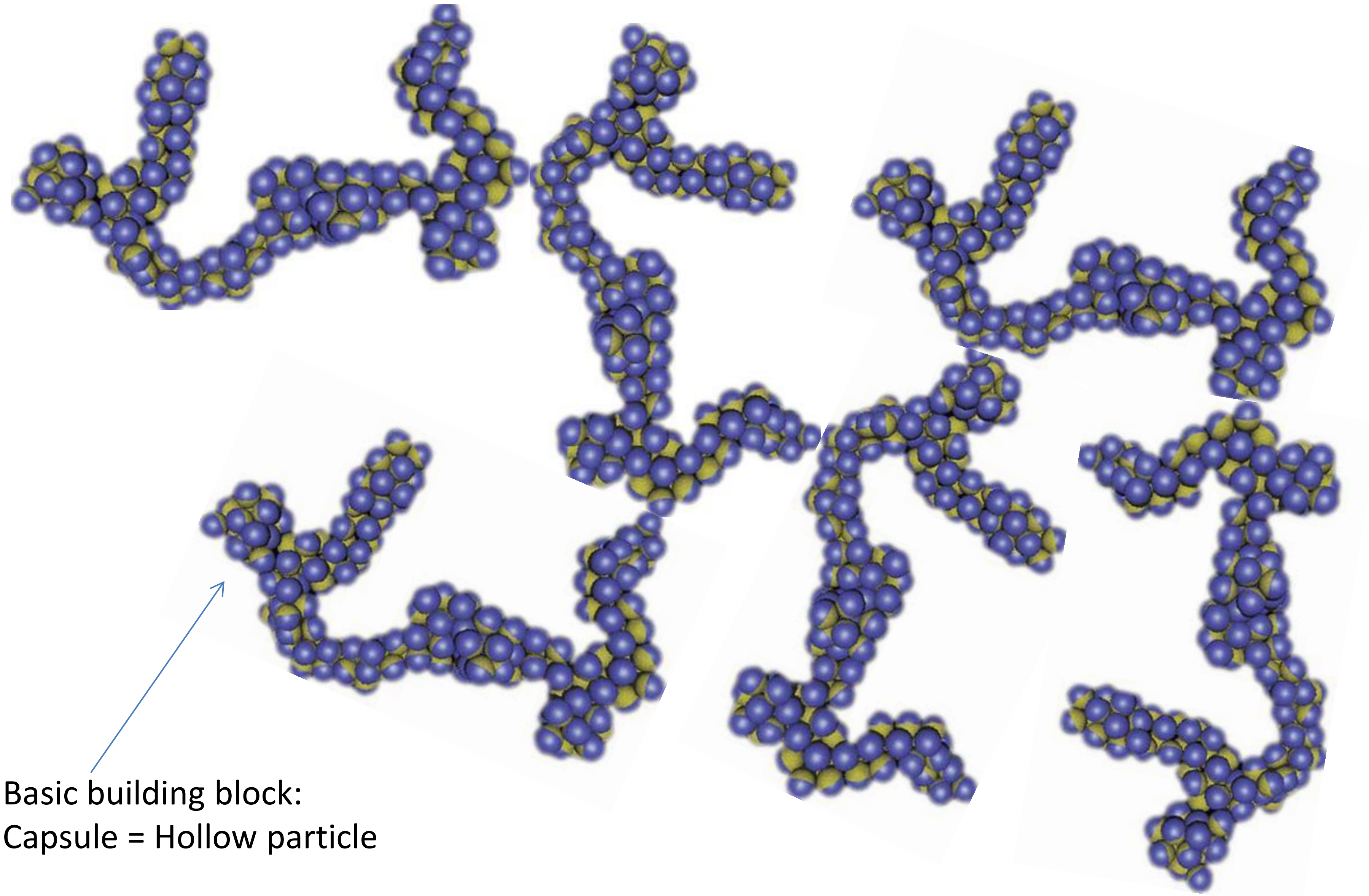




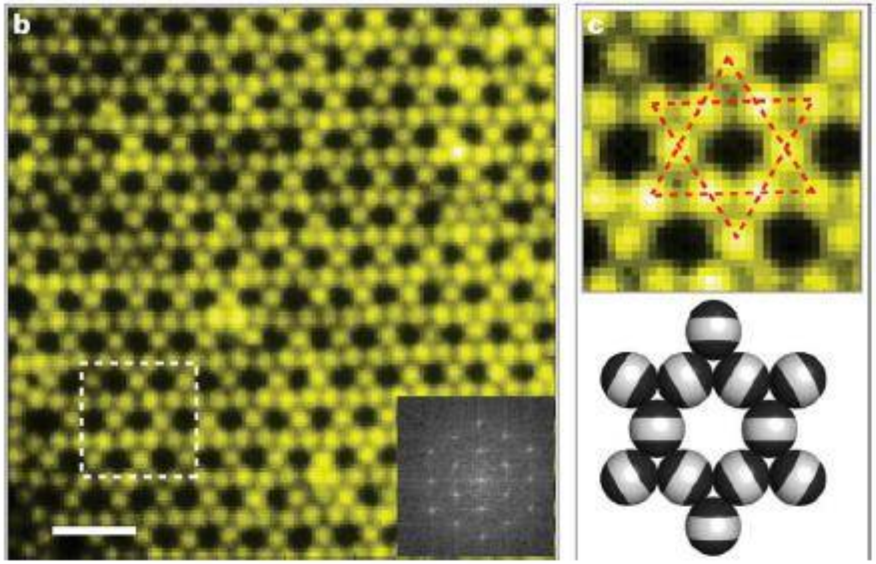
Patchy shells



Future fabrication of **hollow structures?**

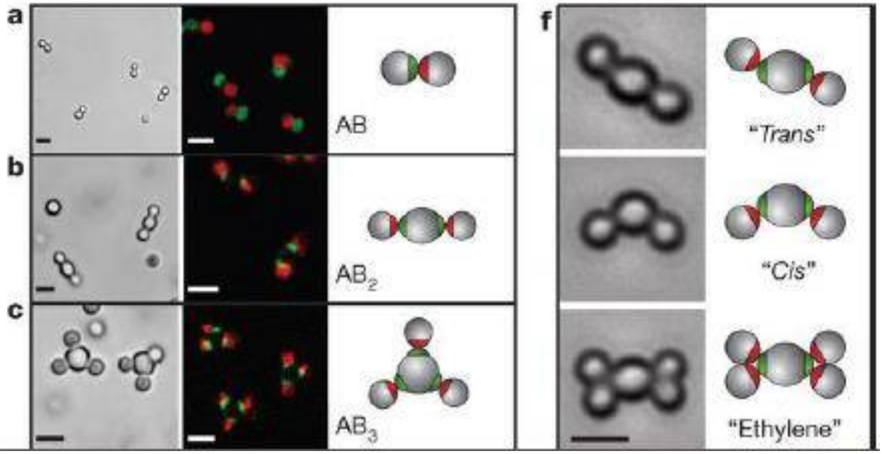


Example of complex hollow structure



Patchy colloidal “molecules”
David Pine Group, Nature 2013

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



Self-assembly into (ordered) structures