Boulder School for Condensed matter and Materials Physics
July 2006

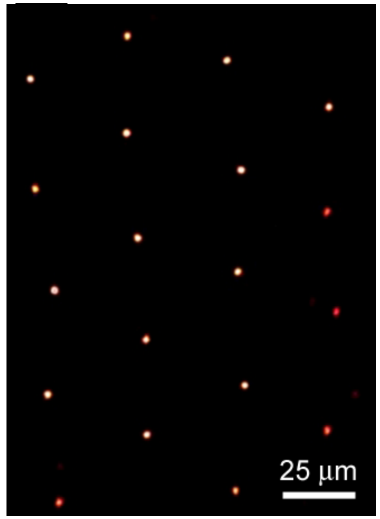
Colloids

- What's a colloid?
- Colloidal Interactions
- Playing with Colloidal Crystals
- Hard Spheres and thermodynamics
- The Crystal – Liquid Transition
- Packings and Candies
- Soft Spheres and electrostatics
- Controlling Colloids with field gradients
- What's new?

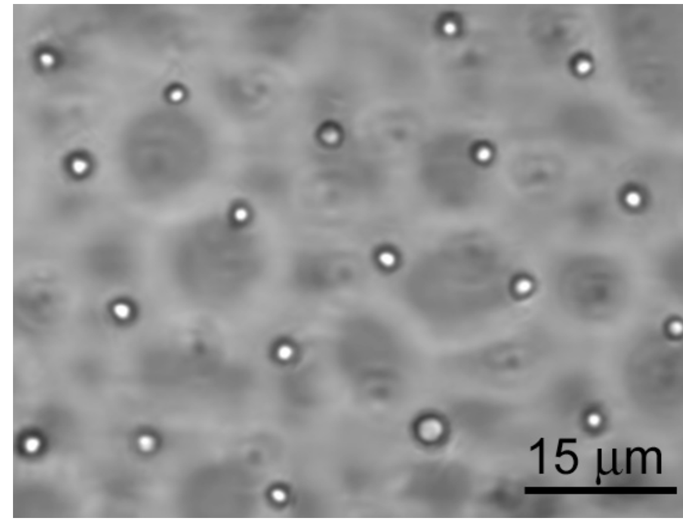
Wigner Emulsions and Crystals
Electrostatics of Oil/Water/Solid Mixtures

3D Colossal Crystals

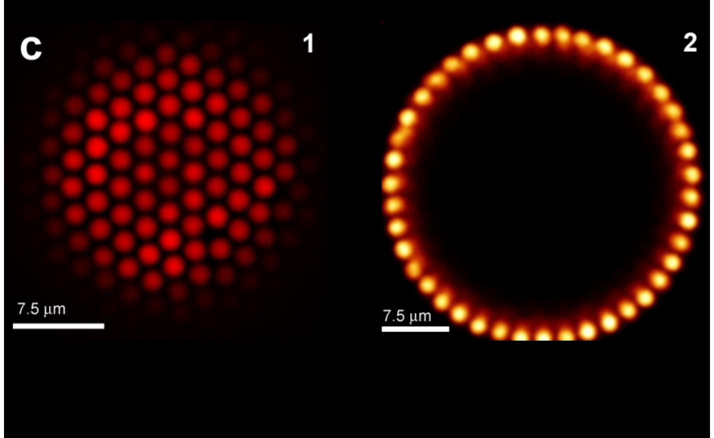
PMMA balls in oil



Water
Droplets
In Oil

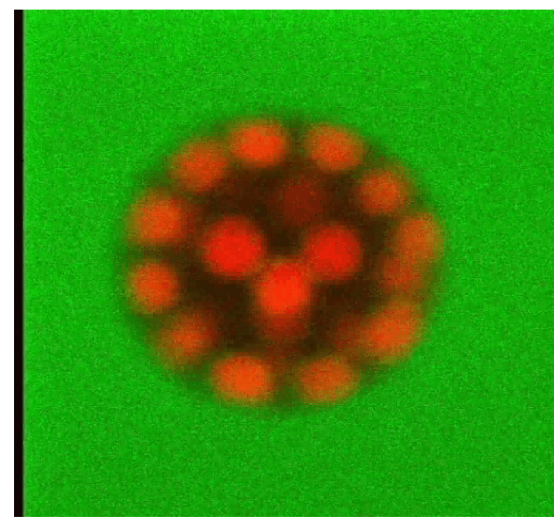


2D Crystals On a sphere



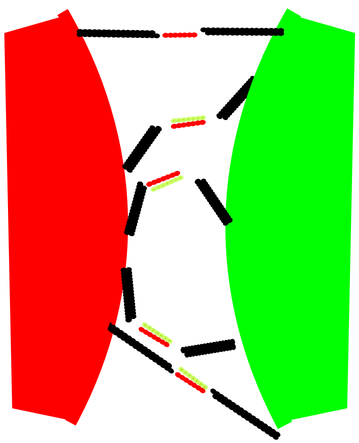
2D interior Crystal

& trapped 3D Crystal

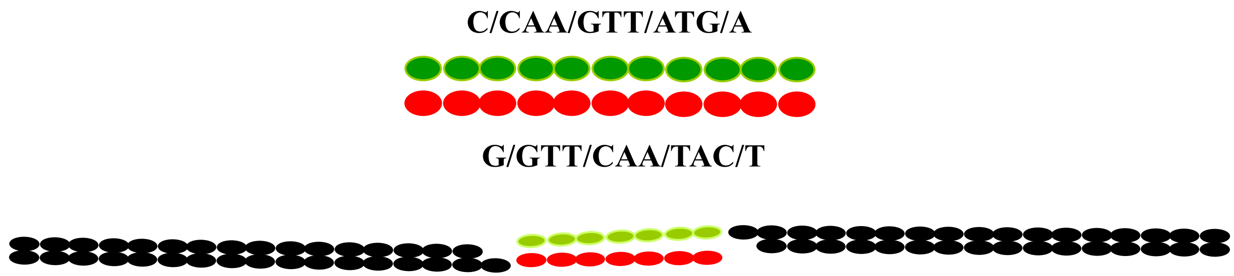


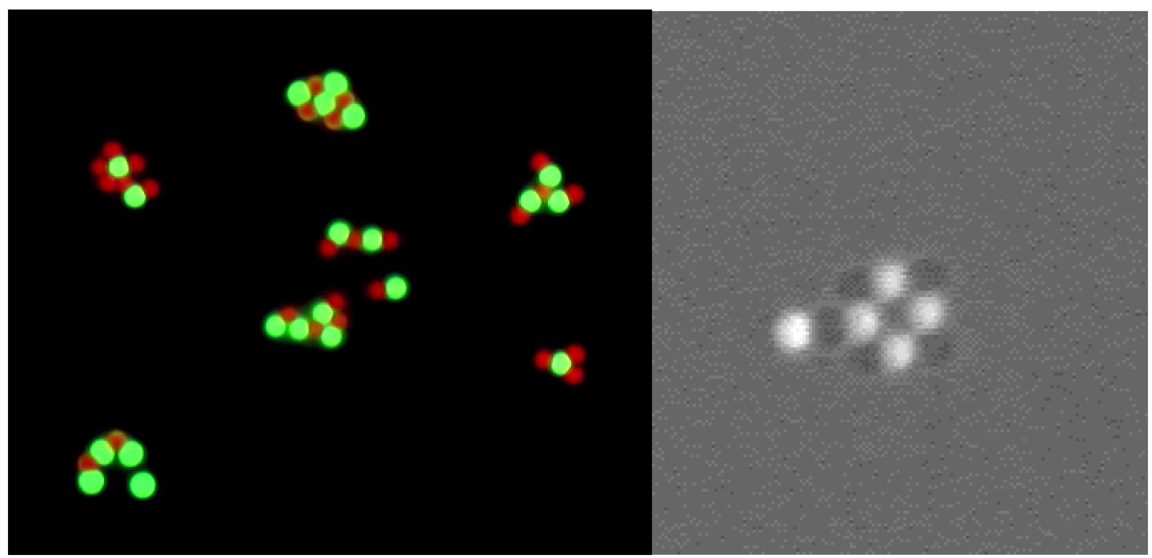
Toward Colloidal Architecture

Building complex stuff, structures, machines



Specific Interactions with DNA



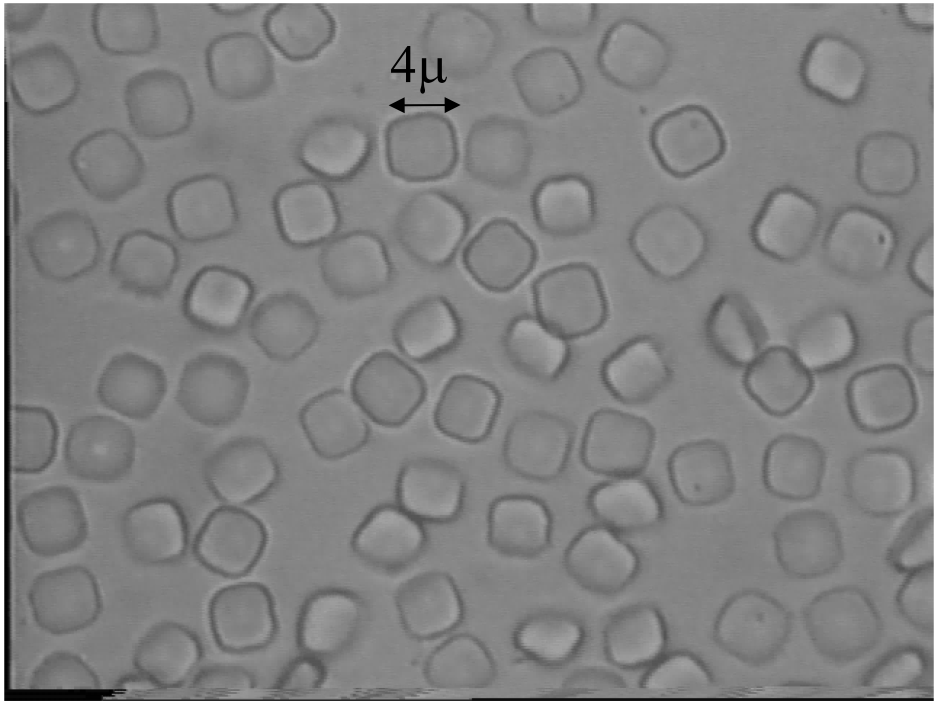


Toward Colloidal Architecture

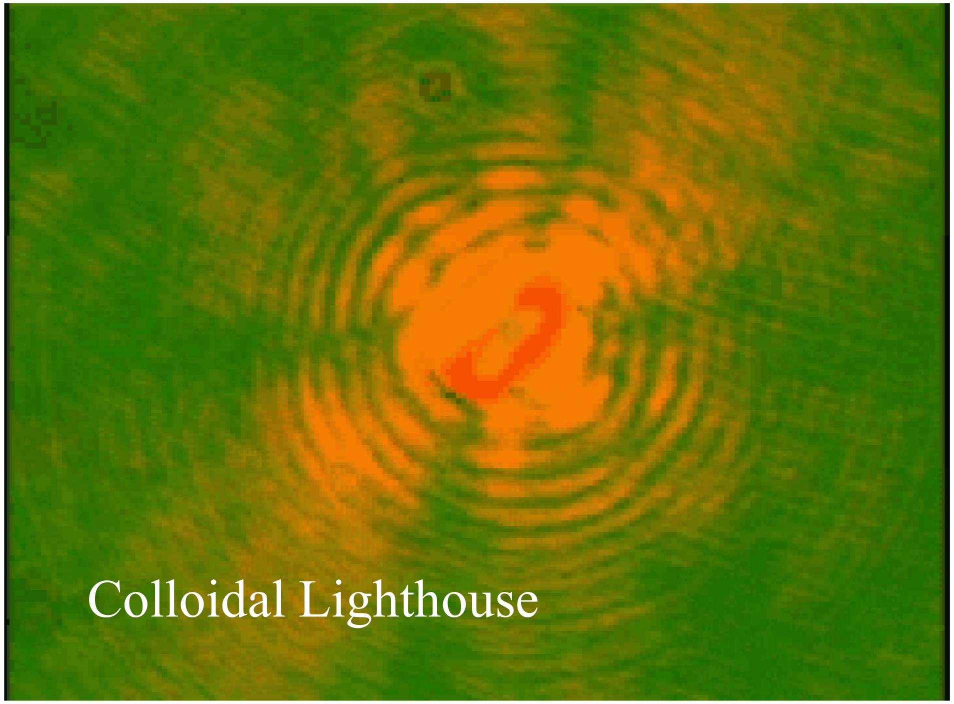
Building complex stuff, structures, machines

Lithographically prepared Colloids

Square Disks in an E field



Disk in circularly polarized light

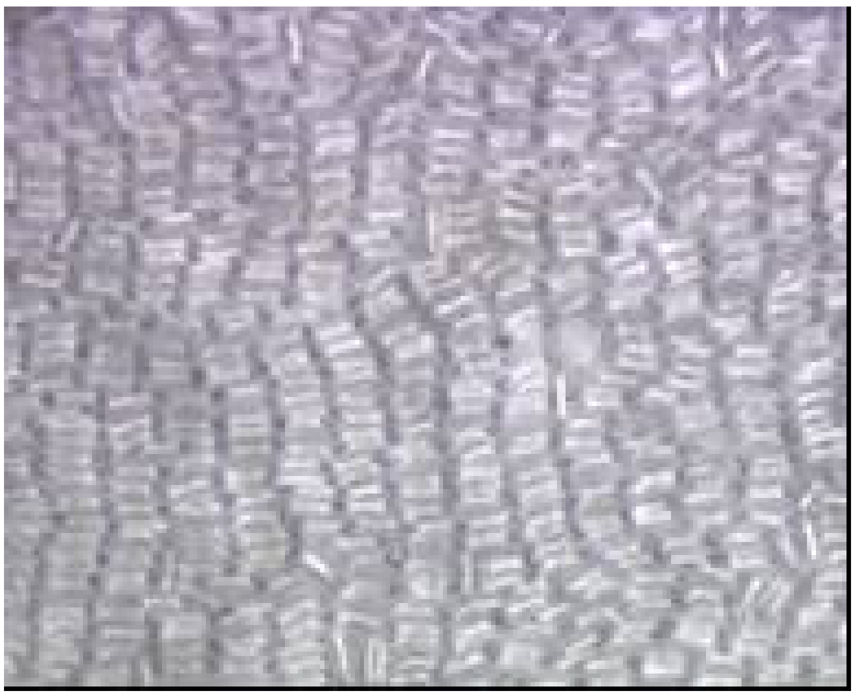


Colloids as Model Systems

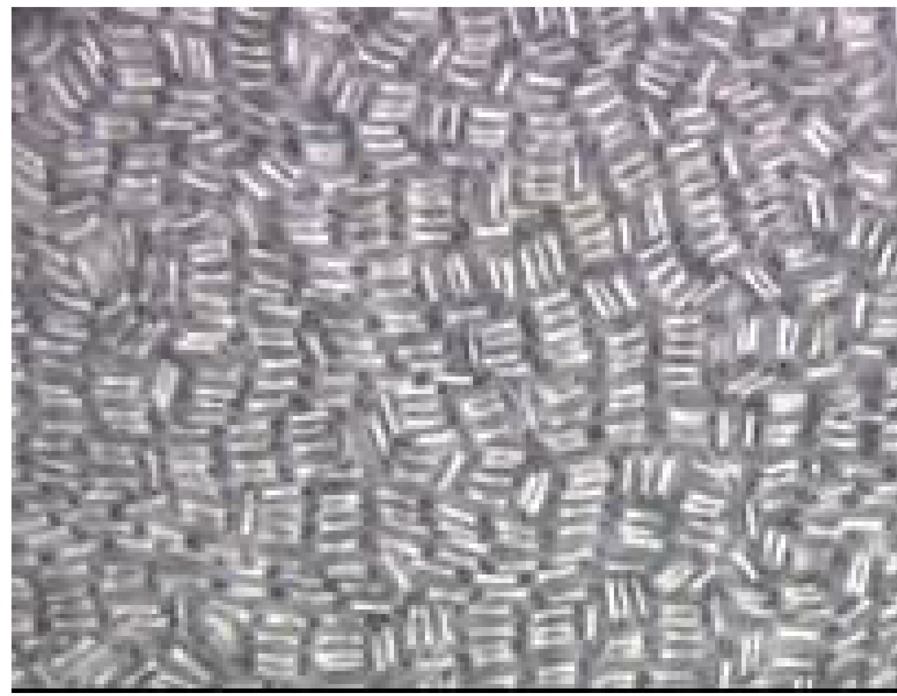
Liquids, crystals, glasses

New Broken Symmetries

2D Smectic - disks on edge, concentrated



2D Tetratic - disks on edge, concentrated



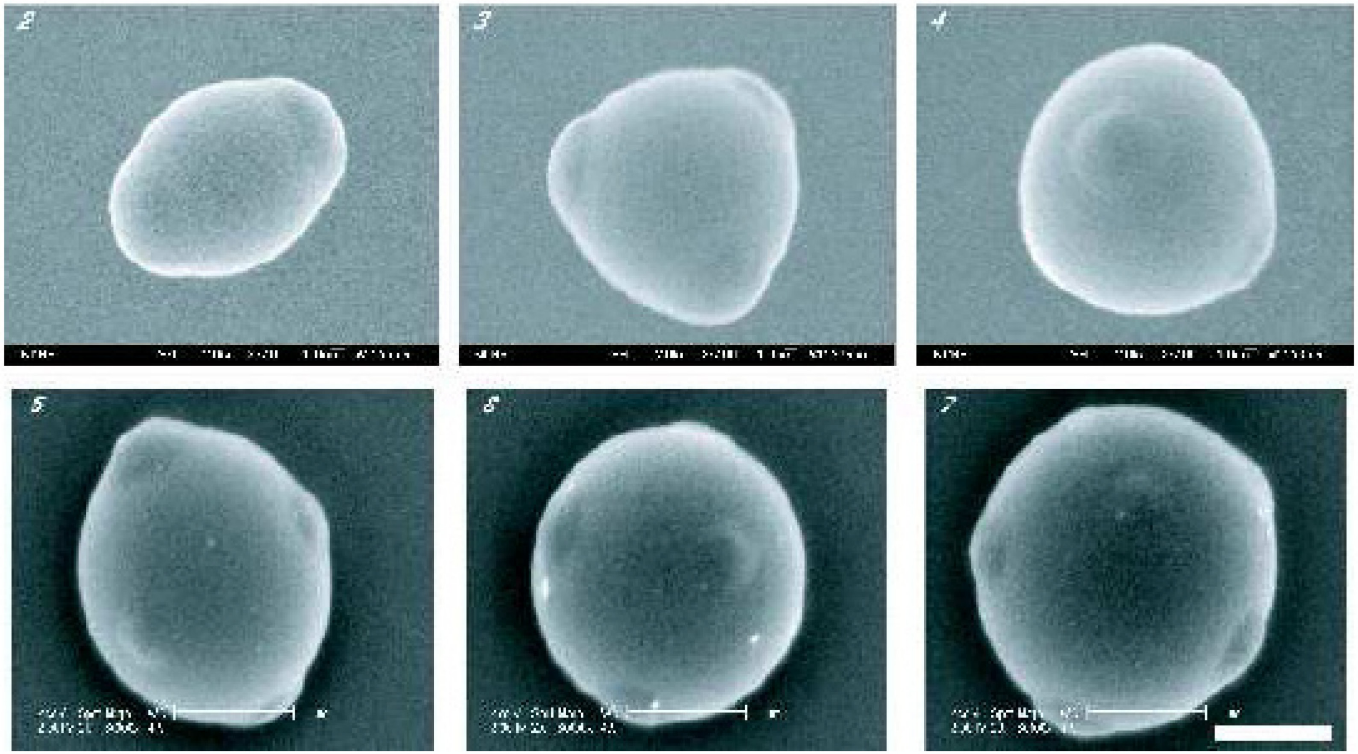


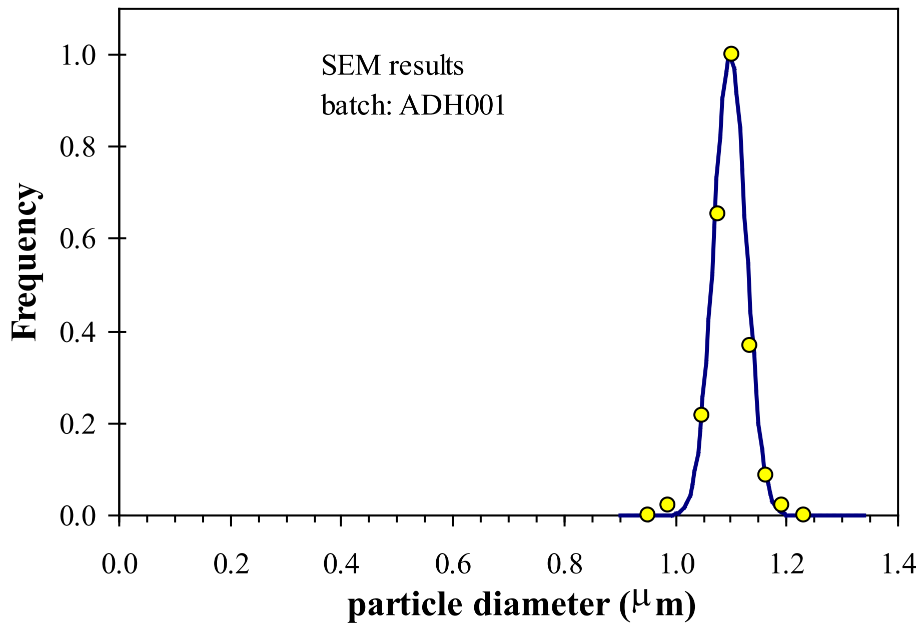
Figure 4: SEM images of colloidal particles with 2 to 7 patches.

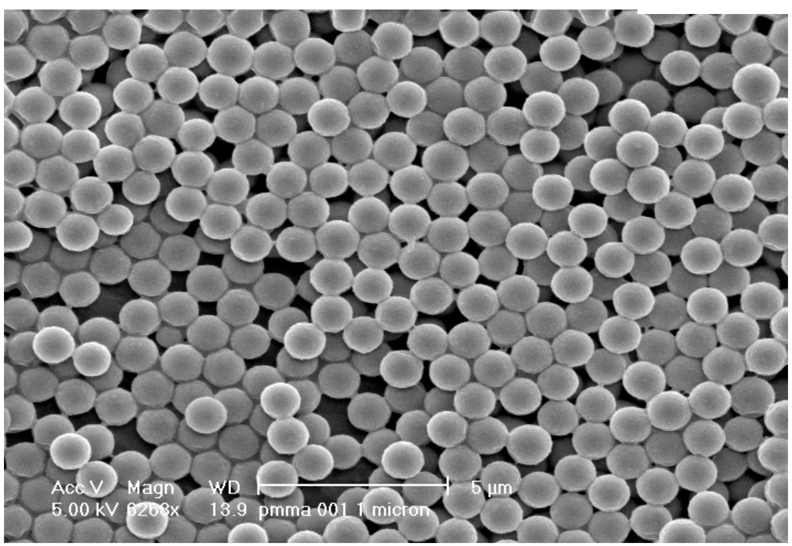
Pine’s Patchy Particles

Andy Hollingsworth

Poly(methyl methacrylate) latices stabilized by

poly(12-hydroxy-steric acid) in nonaqueous media





$$\langle D_p \rangle = 1.098\ \mu m$$

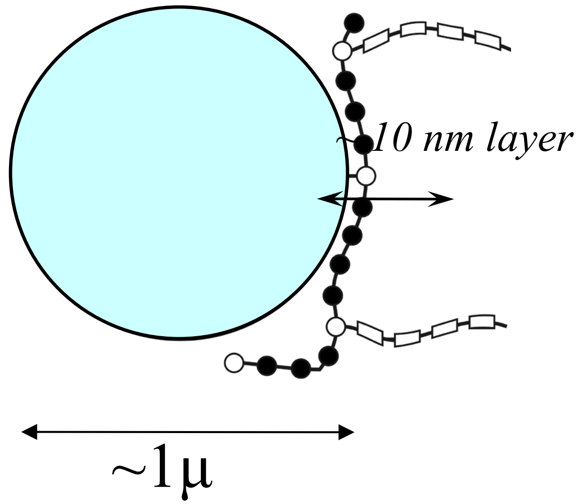
$$\sigma^2 = 0.029$$

$$PDI \equiv \sigma^2 / \langle D_p \rangle = 0.026$$

Polymer Hard Spheres - Colloids in Oil

PMMA-PHSA

Steric stabilization

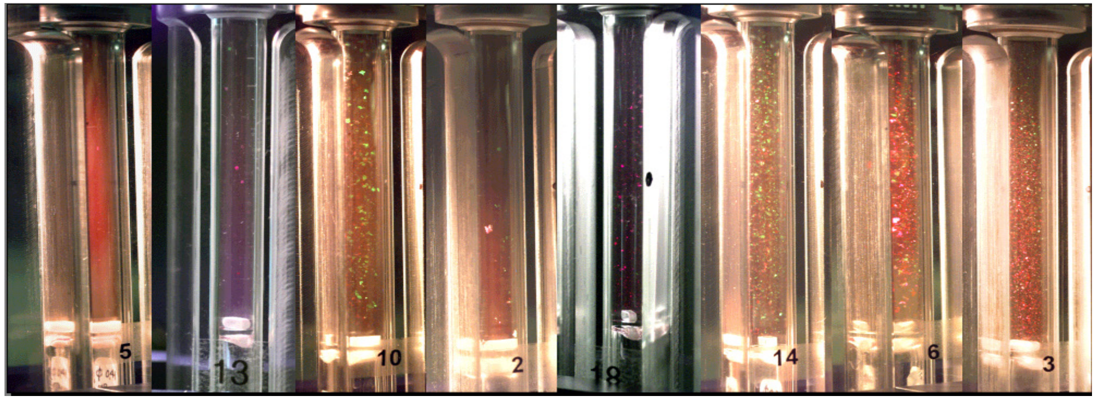


methyl methacrylate (•); methacrylic acid (□); glycidyl methacrylate (○); 12-hydroxystearic acid (▭)

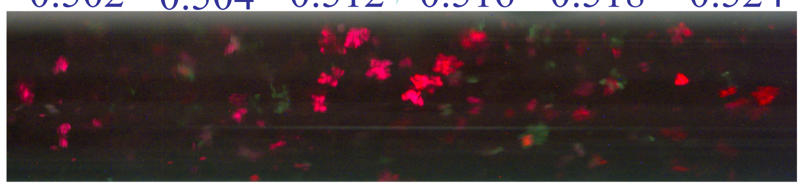
Originally Ron Ottewill - Bristol
ours were from Andy Schofield - Edinburgh
now home grown by **Andy Hollingsworth**

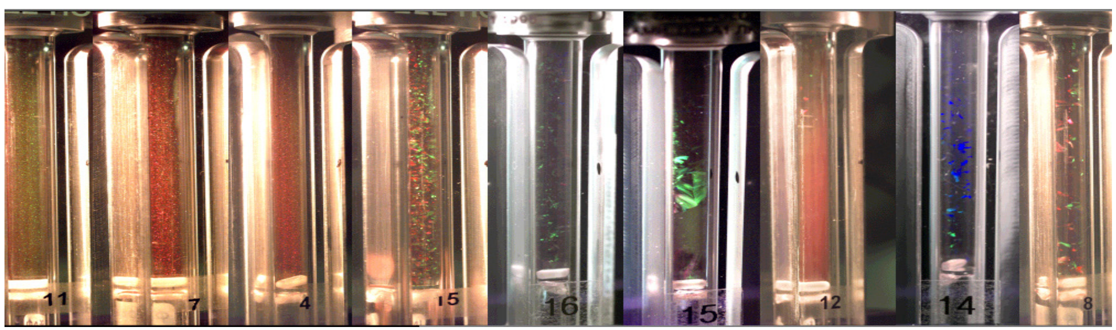

PHaSE
The Physics
of Hard Spheres
Experiment
PHYSICS OF HARD SPHERES EXPERIMENT
PHaSE
NASA LeRC · NYMA · ADF · PRINCETON
NASA
nyma
ADF
Princeton University

CDOT 1998

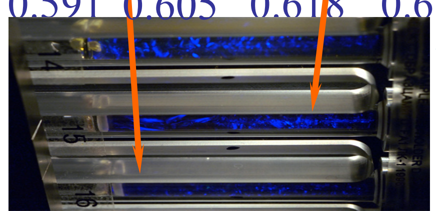


0.50 0.502 0.504 0.512 0.516 0.518 0.524 0.537

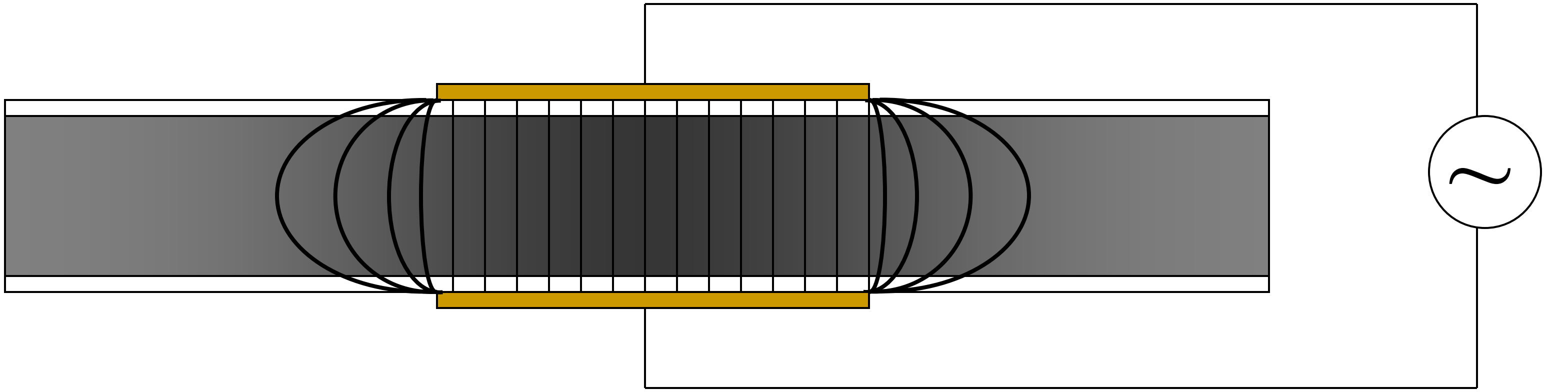




0.547 0.549 0.561 0.591 0.605 0.618 0.619 0.633 0.634



Dielectrophoretic Equilibria to control density



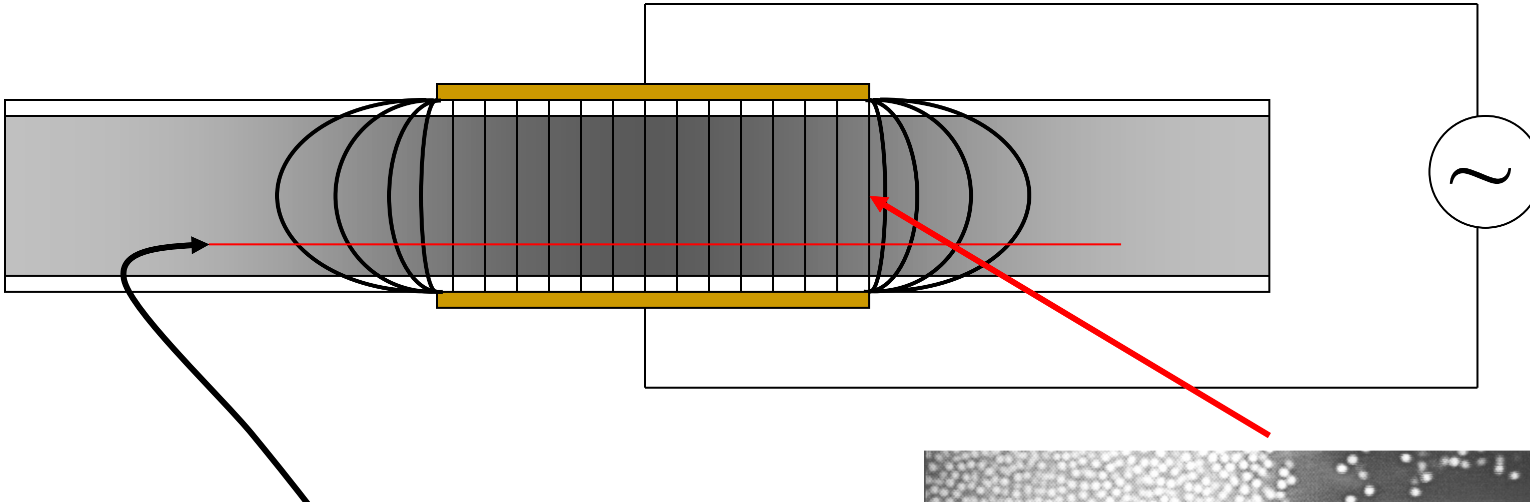
Particles with higher dielectric constant get sucked into region of high electric field

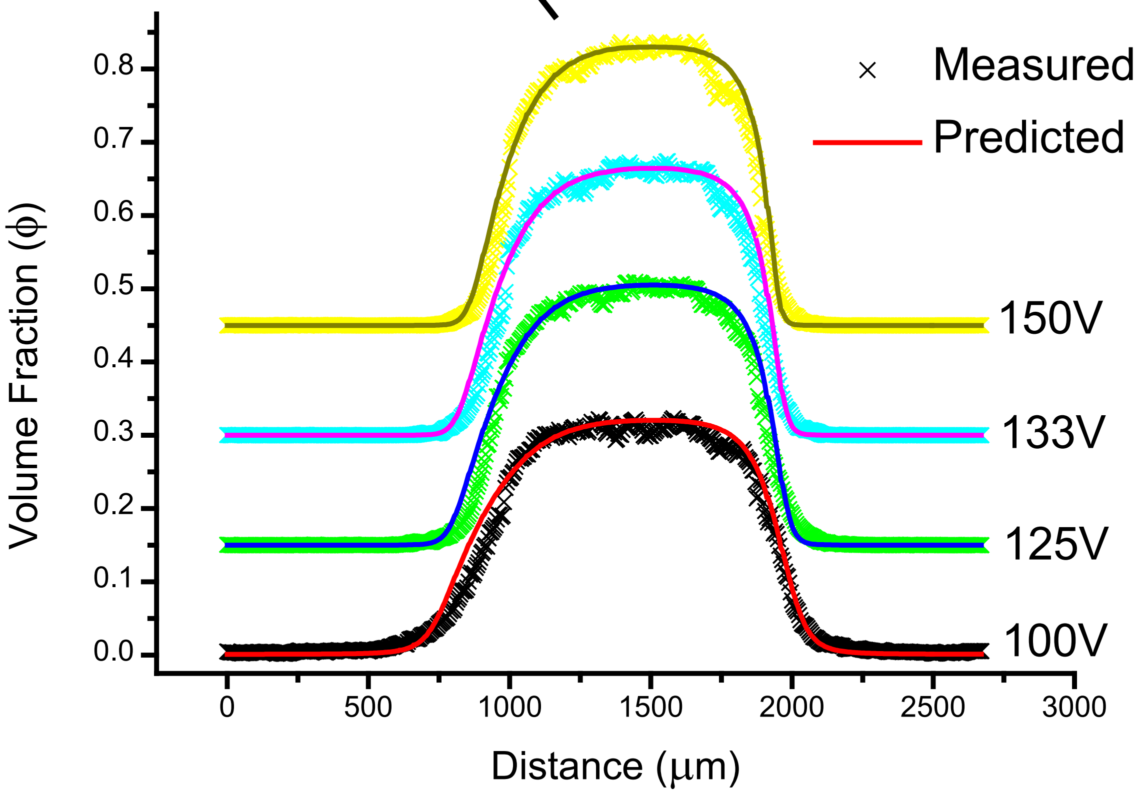
$$\mu(\phi, E) = \mu(\phi, 0) - v_0 \frac{\delta\varepsilon_{eff} E(x)^2}{2} + O(E^4)$$

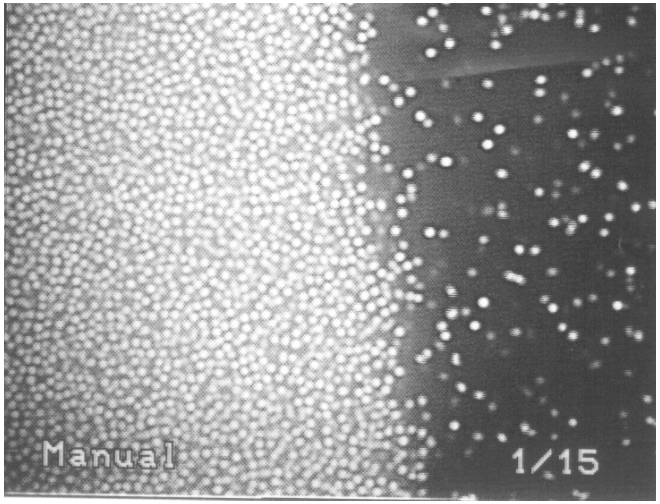
Low density: $\mu = kT\ln(n)$ $\quad n \approx n_0 \exp\left(-\delta\varepsilon_{eff} E^2 \big/ 2k_B T\right)$

Claussius-Mossetti Eq. $\varepsilon_{eff} = 3\beta\varepsilon_m : \beta = (\varepsilon_p - \varepsilon_m)/(\varepsilon_p + 2\varepsilon_m)$

Stable in decalin - tetralin



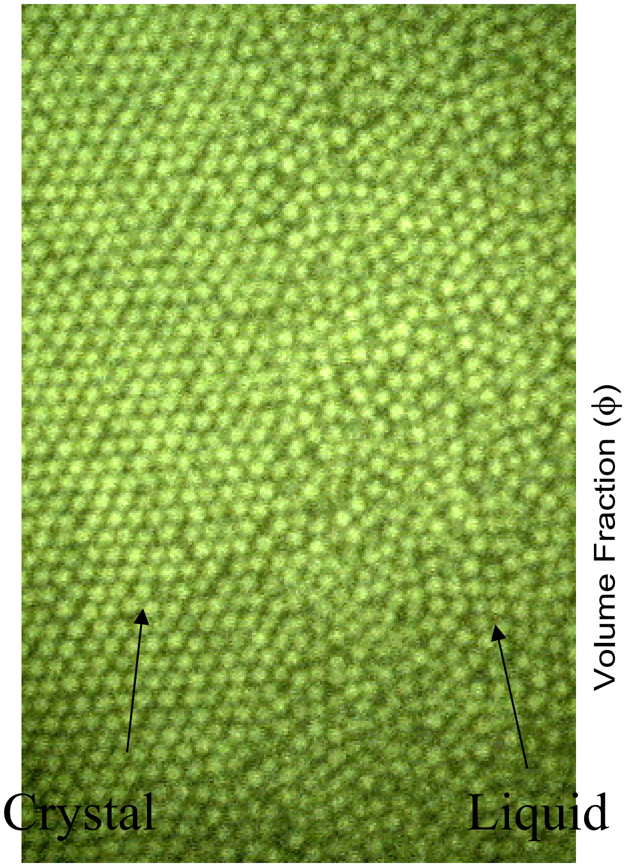




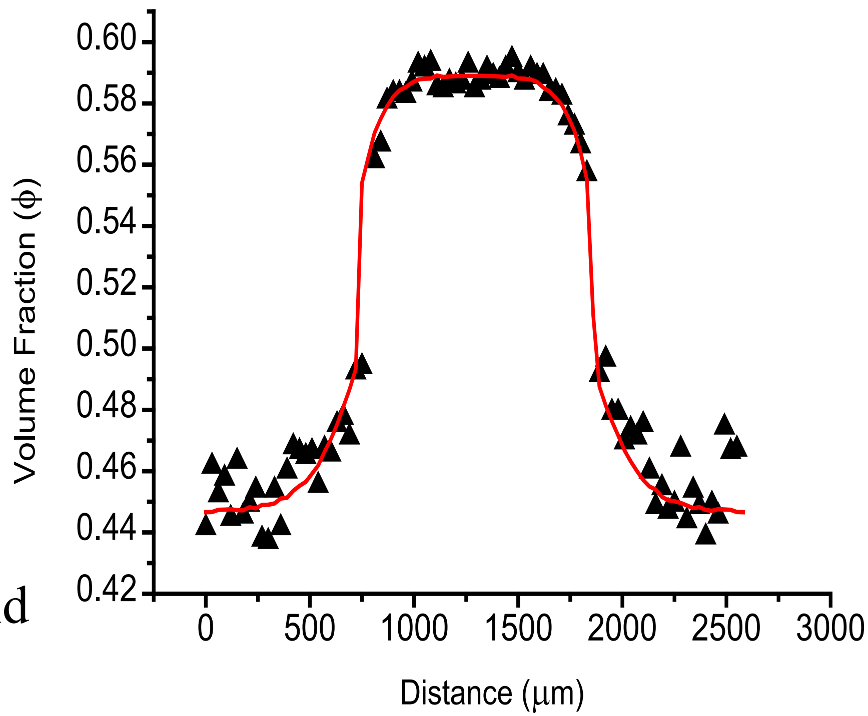
Higher Field
steep gradient

Sullivan, Zhao, Hollingsworth

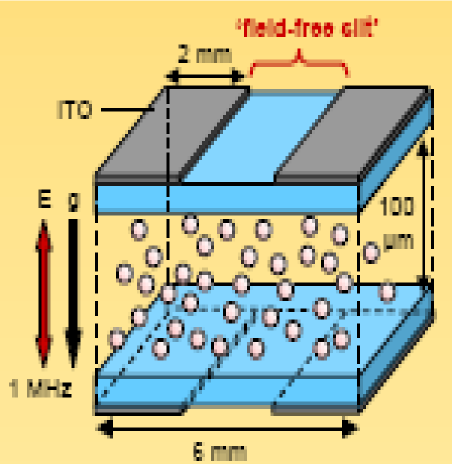
Densification at high volume fraction

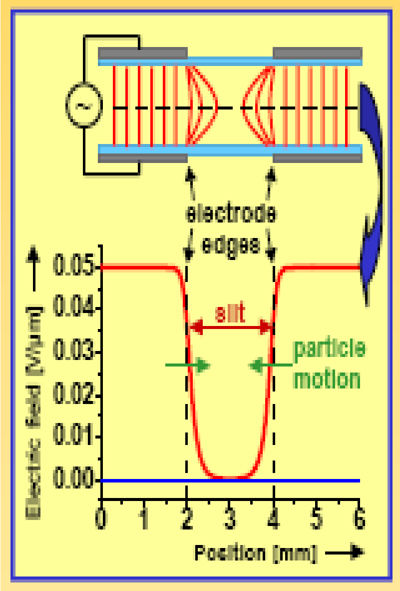


It crystallizes!



Electric Bottle
(e.g. a 3D gate)





Hard Spheres

Saturating the solvent with the **salt** tetrabutylammonium bromide (~ 260 µM) screens the particle charges and causes **hard sphere like behavior** ($\kappa^{-1} \approx$ 90 nm, $\kappa a \approx 12$).

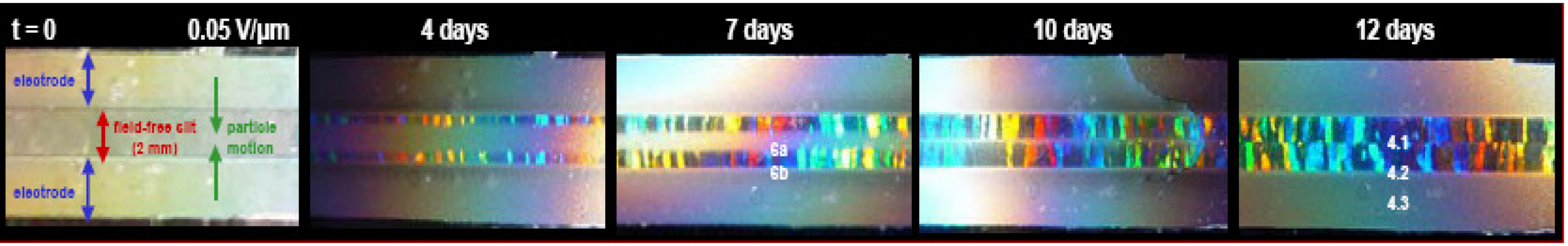
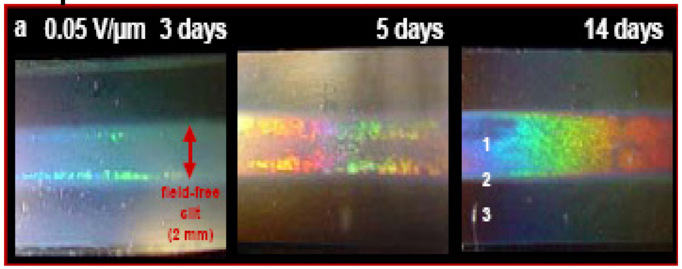
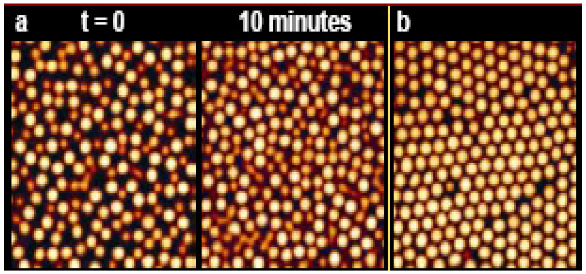


Fig. 6 Growth mechanism A bleached rectangle in one of the growing crystalline bands (E = 0.05 V/µm) indicates how the entire crystal moves into the field-free slit (~ 0.5 µm/hour), while it grows both at its inner and outer edge. a) Inner edge (slit center to the left) and b) outer edge (electrode edge to the right), as indicated in fig. 3 (day 7).

Soft Spheres



Glasses

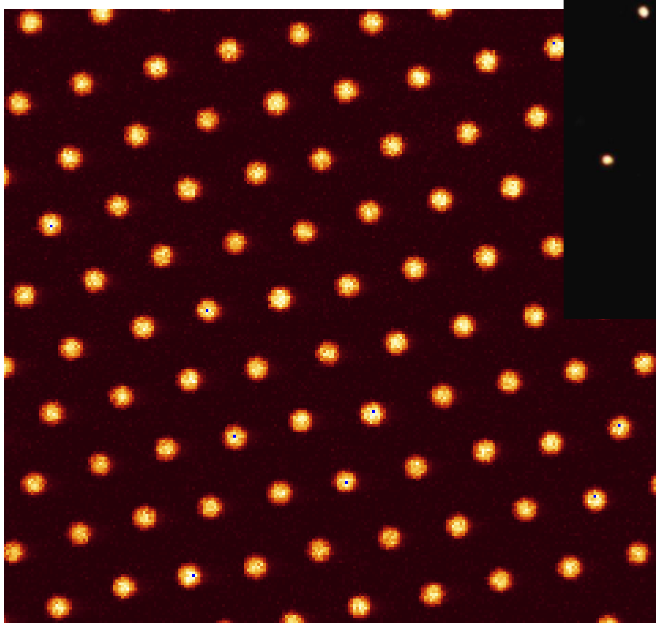


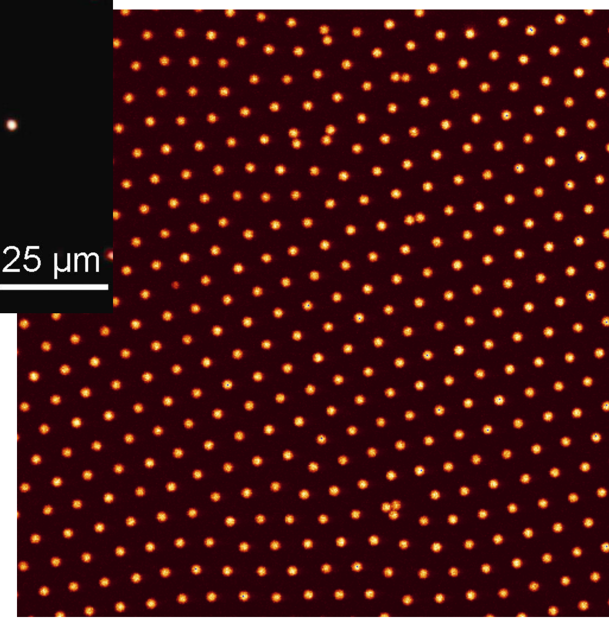
fast slow

Leunissen, Sullivan, van Blaaderen, Utrecht, NYU

Tried to density match PMMA “hard spheres” in decalin – CHB (cyclohexylbromide)

Instead get charge stabilized colloid in ***oil,*** and screening length is enormous, $\lambda > 30\mu$





Part of a (110) plane of the body-centered-cubic crystal in the bulk oil phase.

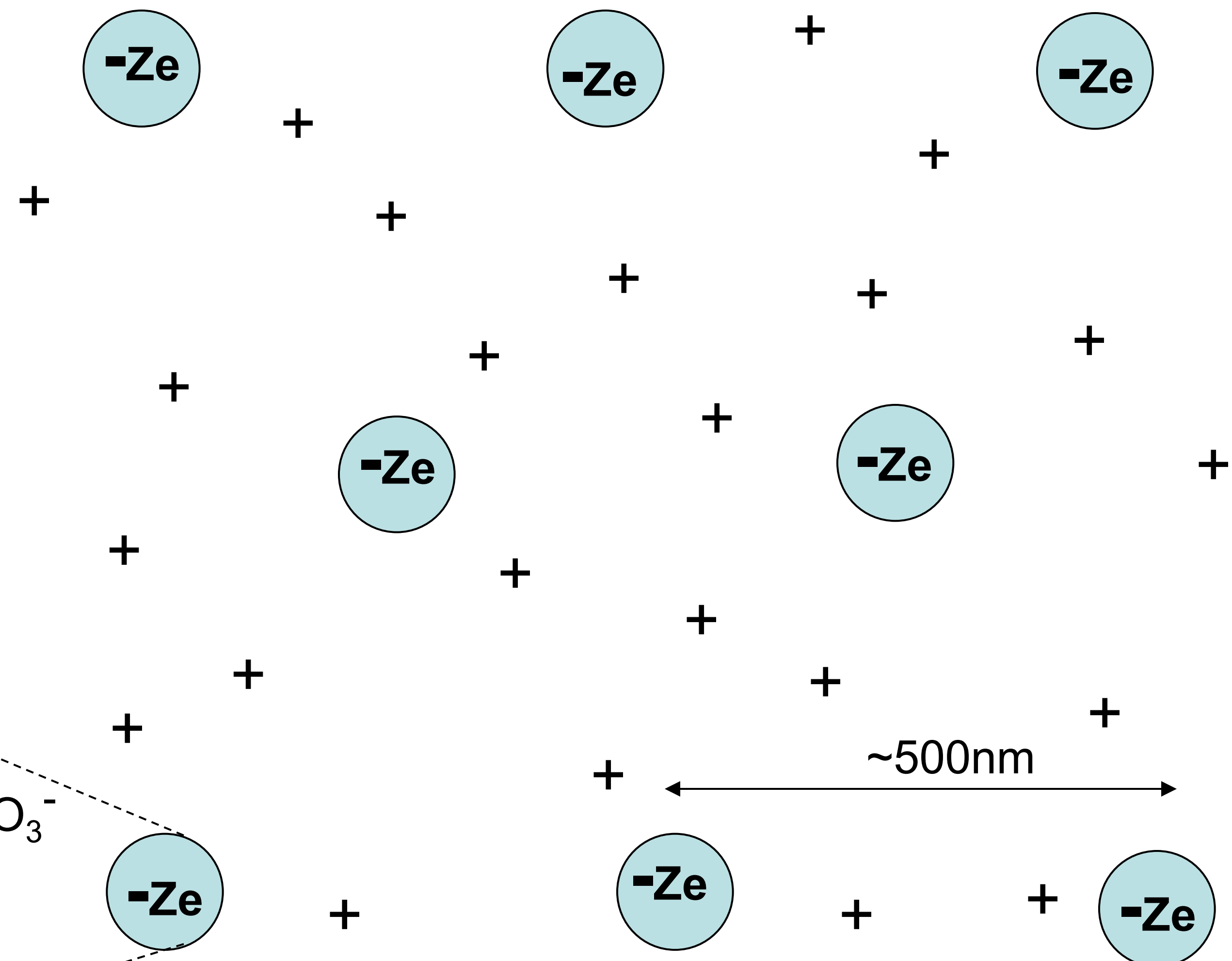
30μ

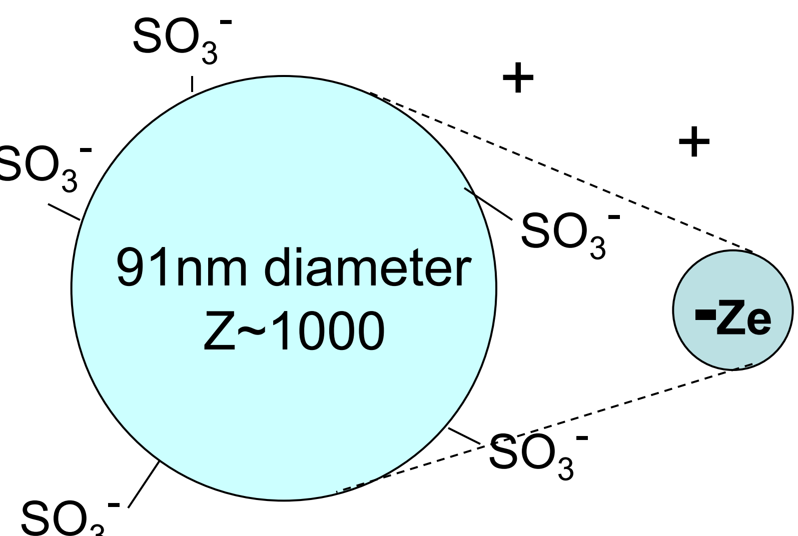
Coulomb crystals – ***BCC*** lattice

Van Blaaderen - Utrecht

Colloidal Crystals - Polyballs

Polystyrene Spheres in Water





~1% colloids

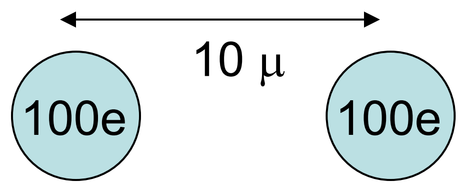
Electrostatic interactions

Bare

$$\frac{e^2}{\varepsilon_0 r} = .69 k_B T$$

Single electron charge,
r=1 micron, room temp

$$\frac{Z^2 e^2}{\varepsilon\ r} = 230 k_B T$$



ε=30

(water ε=80, decalin ε=3)

Screened by conducting ions/electrons

$$\frac{Z^2 e^2}{\varepsilon\ r} e^{-r/\lambda}$$

Yukawa Potential

Colloids

Debye Length

$$\lambda^{-2} = \frac{4\pi n_{ions} e^2}{\varepsilon k_B T}$$

Metals

Thomas-Fermi length

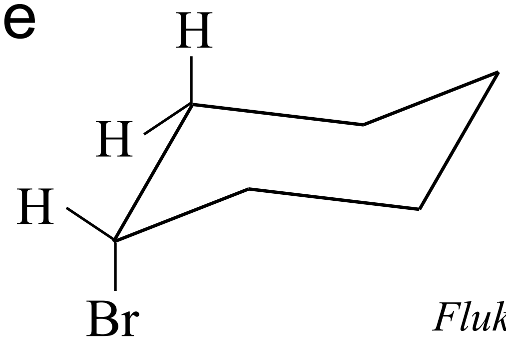
$$\lambda^{-2} = \frac{4\pi n_{els} e^2}{\varepsilon_0 k_B T_F}$$

Typical screening length: 1 milliMole NaCl in water λ=10nm

Why do they charge?

Pure solvent properties, 25 °C

cyclohexyl bromide



$\varepsilon_{\infty} = 7.9$

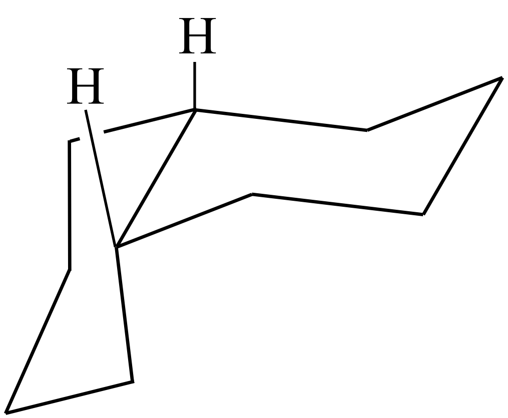
$\eta = 2.06$ cP

$n_D = 1.4933$

$\rho = 1.330\ \mathrm{g/cm^3}$

Fluka lot no. 436684/1, 99.5% assay

cis-bicyclo[4.4.0]decane
(*cis*-decalin)



$\varepsilon_{\infty} = 2.2$

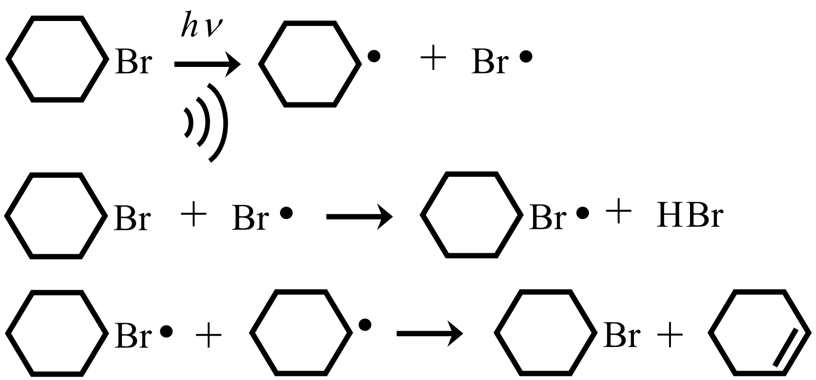
$\eta = 3.05$ cP

$n_D = 1.4792$

$\rho = 0.8929\ \mathrm{g/cm^3}$

99% assay, used as received

Particle charging mechanism
(proposed, no added salt)



homolytic cleavage of halogen-carbon bond

propagation and termination reactions

$$2\,Br^{\bullet} \longrightarrow Br_2$$

free radicals

$$HBr \rightleftarrows H^{+} + Br^{-}$$

weak acid

$$H^{+}\ (H_3O^{+})\ \text{- - -}\ O = COH\cdot(CH_2)_{10}CH\cdot C_6H_{13}$$

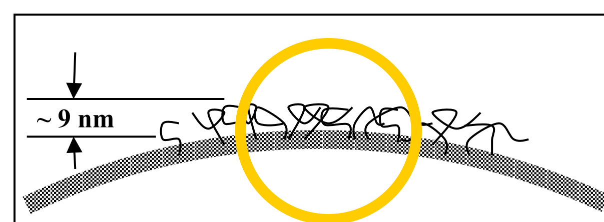
$$O = CO\cdot(CH_2)_{10}CH\cdot C_6H_{13}$$

$$O = CO\cdot(CH_2)_{10}CH\cdot C_6H_{13}$$

$$OR$$

ion-dipole association

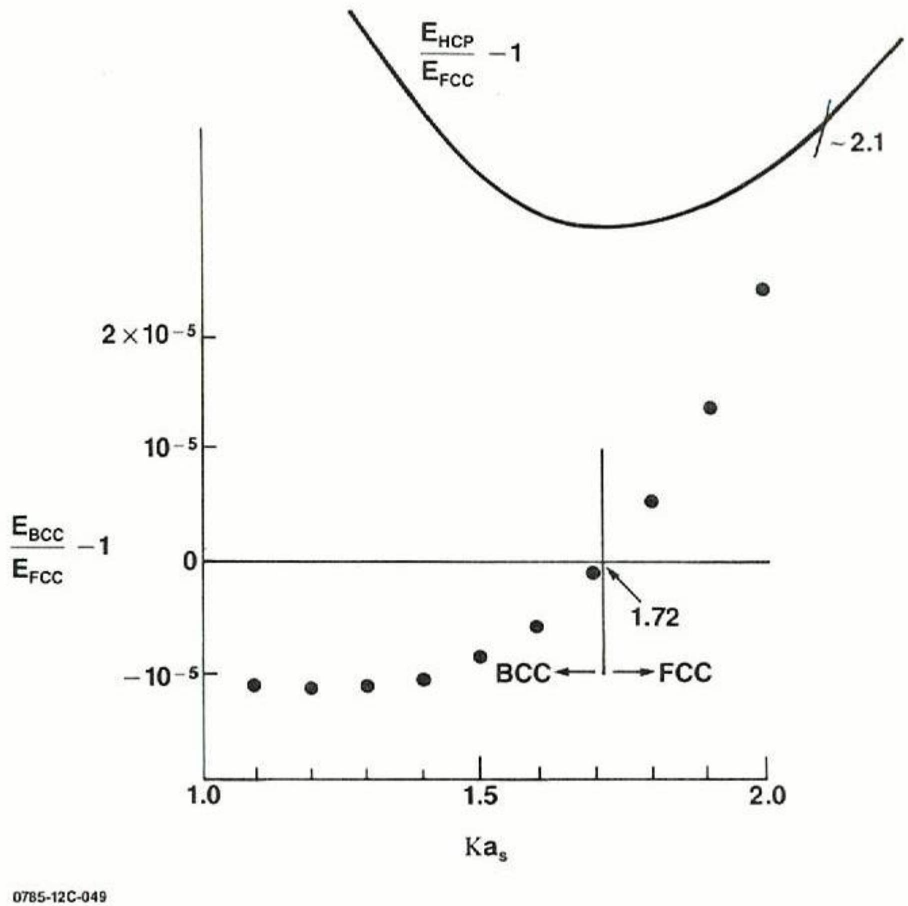
poly(12-hydroxy stearic acid) $M_N \sim 1700$



Why is screening length so large?

$$\frac{Z^2 e^2}{\varepsilon r} e^{-\kappa r} \qquad \kappa^2 = \frac{4\pi n_{ions} e^2}{\varepsilon k_B T}$$

Yukawa Potential



BCC → $\kappa a_s < 1.72$

$a_s \sim 35\mu m$, $\kappa^{-1} > 20\mu m$

$\kappa^{-1}_{calc} \sim 30\mu m$
from $n_{counterion}$ and ε

→ No other ions

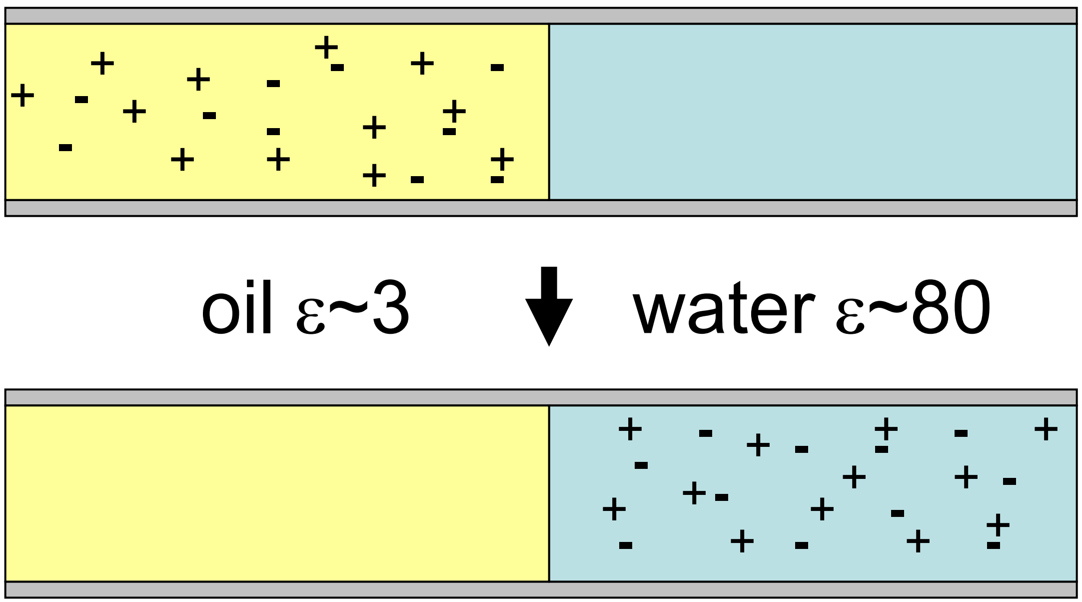
C_{ions} ~ 10 picomolar
Z~500

History

1957	Williams + Smith	Tipula Iridescent Virus
1959	Klug, Franklin eTal.	Structure
1968	Woods eTal.	Polystyrene Spheres
1969	Hiltner + Krieger	Bragg Scattering
1974 76	Williams + Crandall + Wojtowicz	Structure, Melting
1974	Kose, Hachisu eTal.	Bragg Scattering
1975	Schaefer + Ackerson	Dynamic Light scattering
1977	Mitaku eTal.	Shear properties with ultrasound
1978	Pieranski eTal	Dislocations, Shear Mod. 2-dim.
1979	Clark eTal.	Shear melting

Only get colossal crystals in some samples.

What's different? ---------- Water?



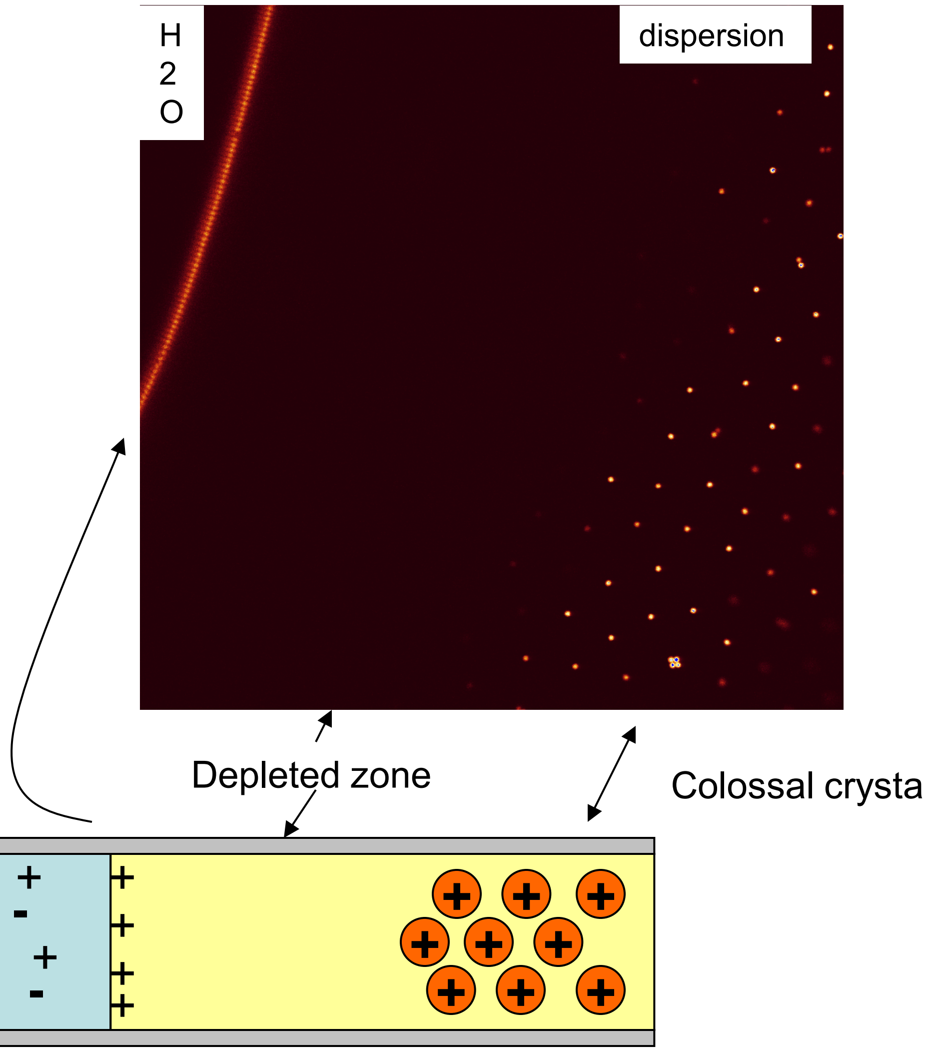
water has much higher ε

should suck ions out of oil

$$E = -\frac{\varepsilon E^2}{2}$$

Add water to half of cell

Confocal view of a layer in the cell

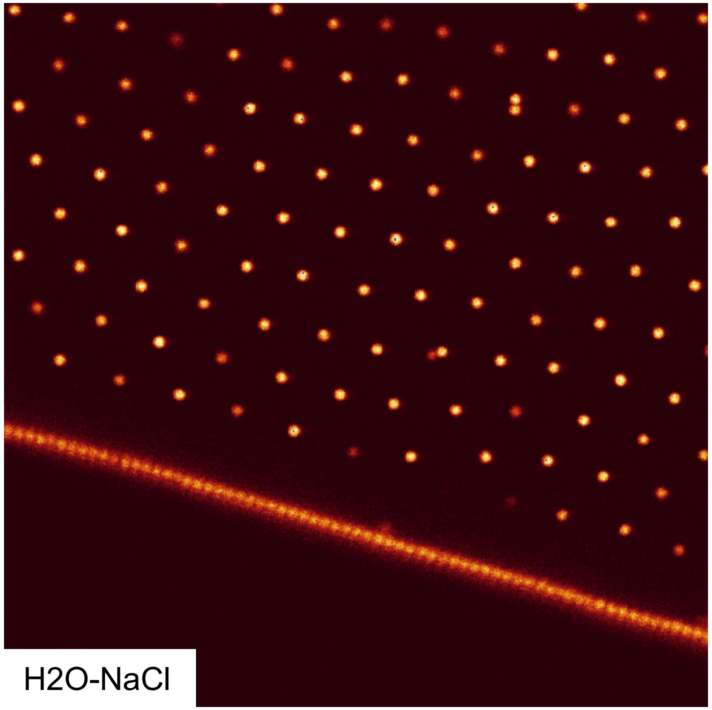


Depletion zone
→Water droplets are charged positive

Why is water charged?

Water preferentially pumps H^+

ion	Hydration energy KJ/M
OH^-	-437.5
H^+	-1099
Br^-	-326.6



Charge at interface depends on salt, pH….?

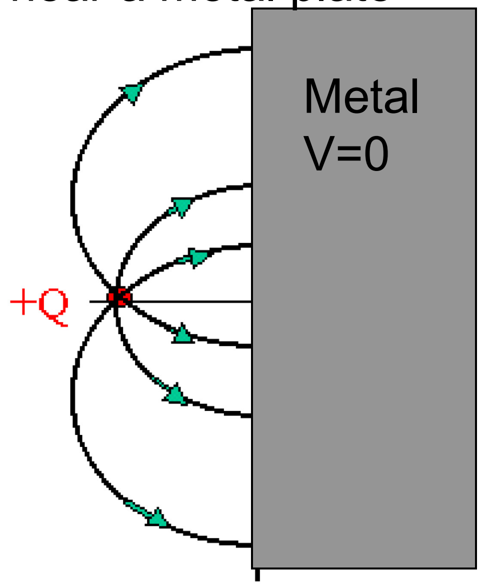
No/small depleted zone

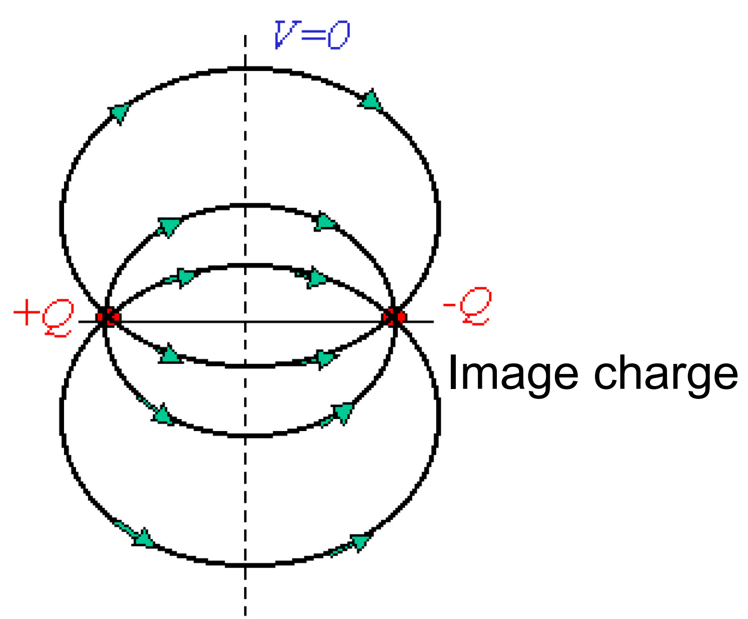
Note also particle accumulation at interface?

CHB-decalin dispersion in contact with NaCl saturated water in 50/50 filled capillary

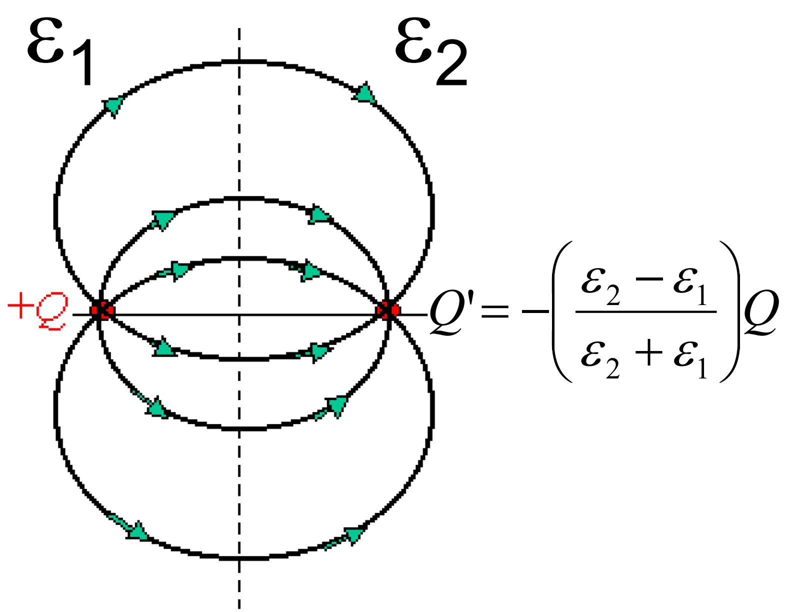
Image charges

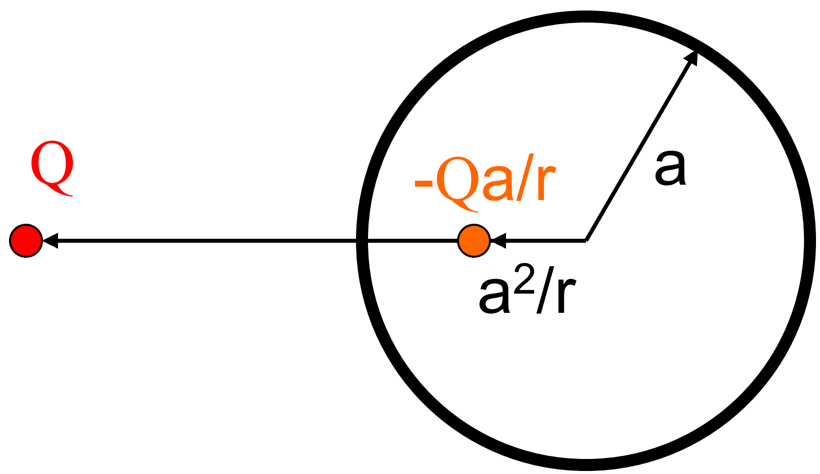
Charge near a metal plate





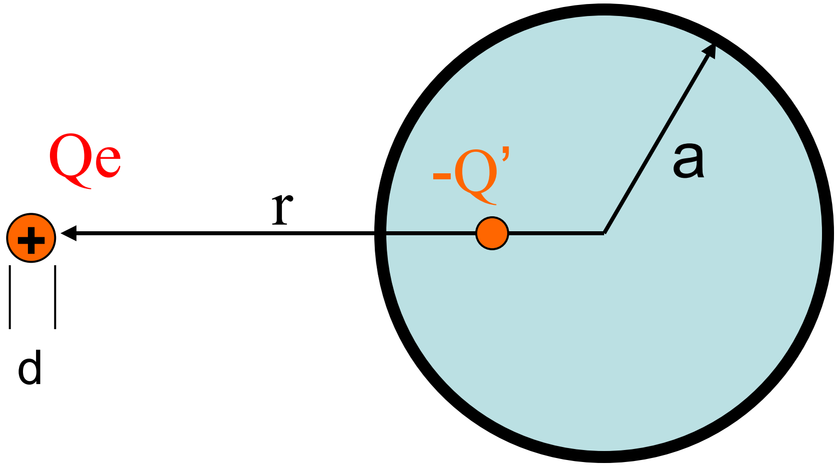
Charge near a dielectric



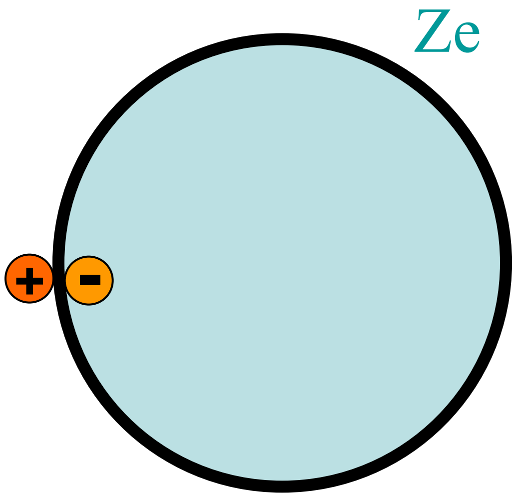


Charge near a conducting sphere

Image charge "colloidosome"

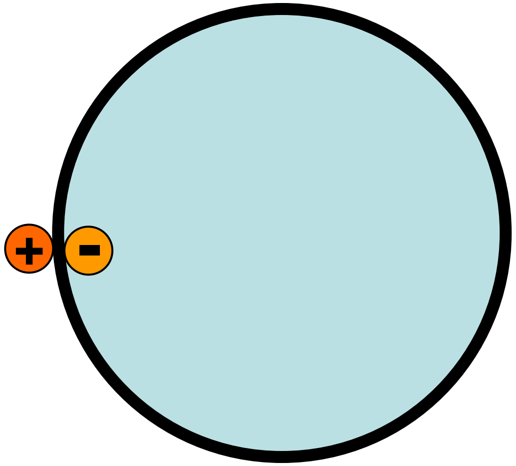


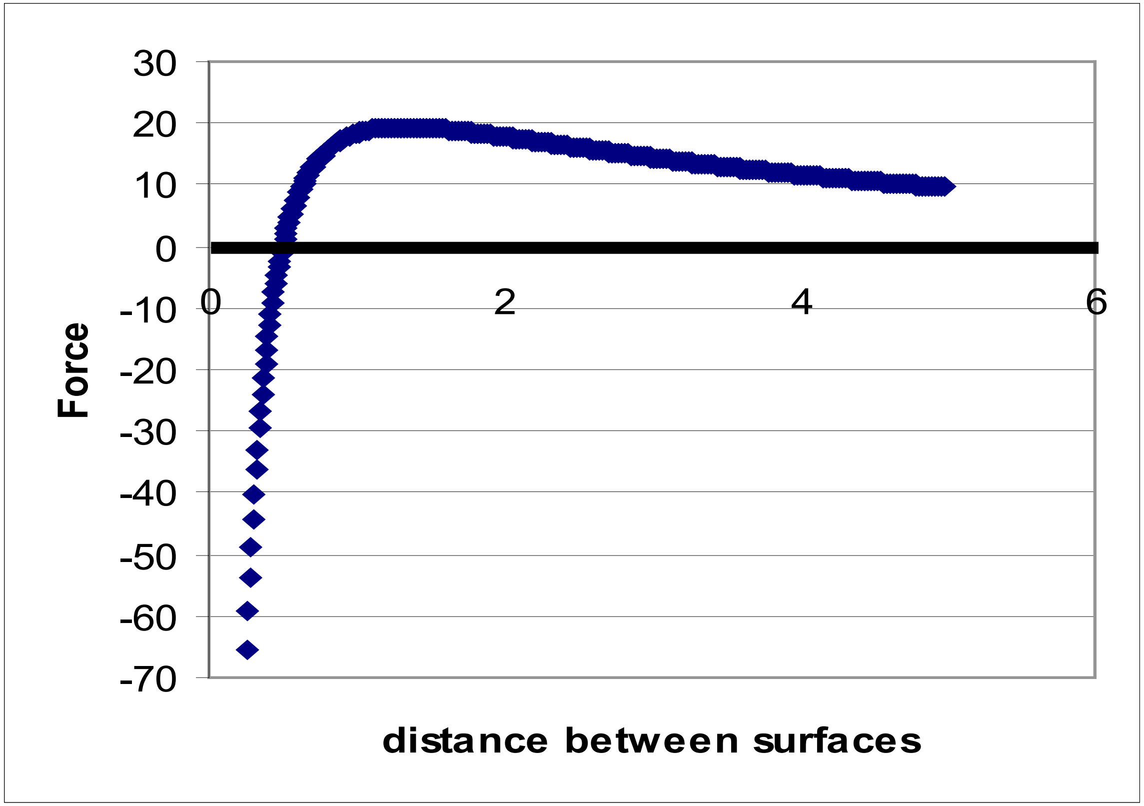
$$E = \frac{ZQe^2}{r} - \frac{Q^2e^2a}{r^2 - a^2}$$



$$F = \frac{ZQe^2}{(r + d/2)^2} - \frac{Q^2e^2}{d^2}$$

Image charge colloidosome





Particles attracted to droplet

but there is a barrier

From Jackson - Electrodynamics

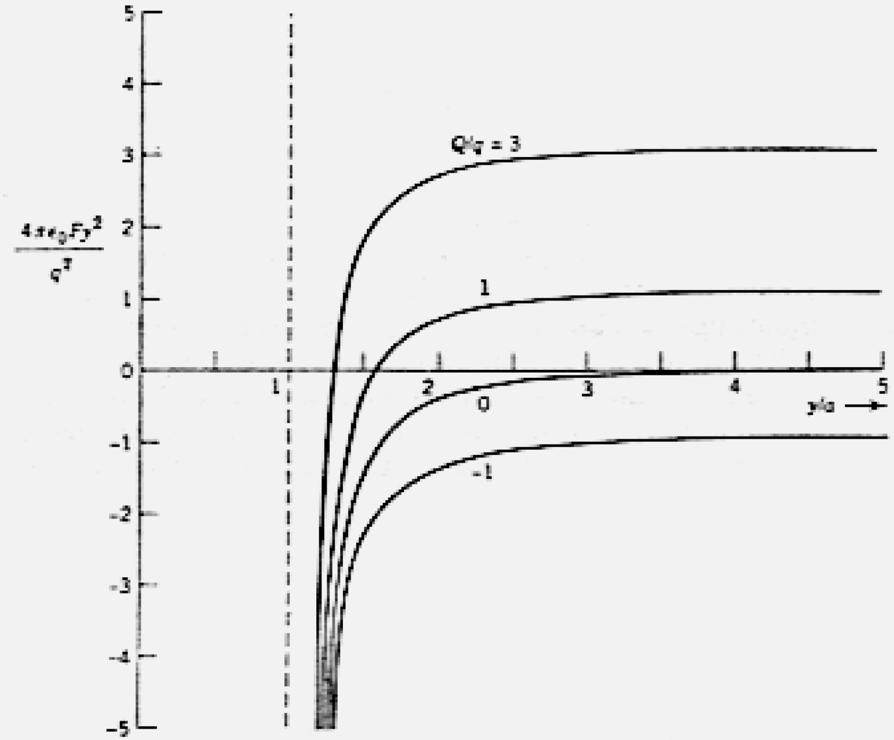
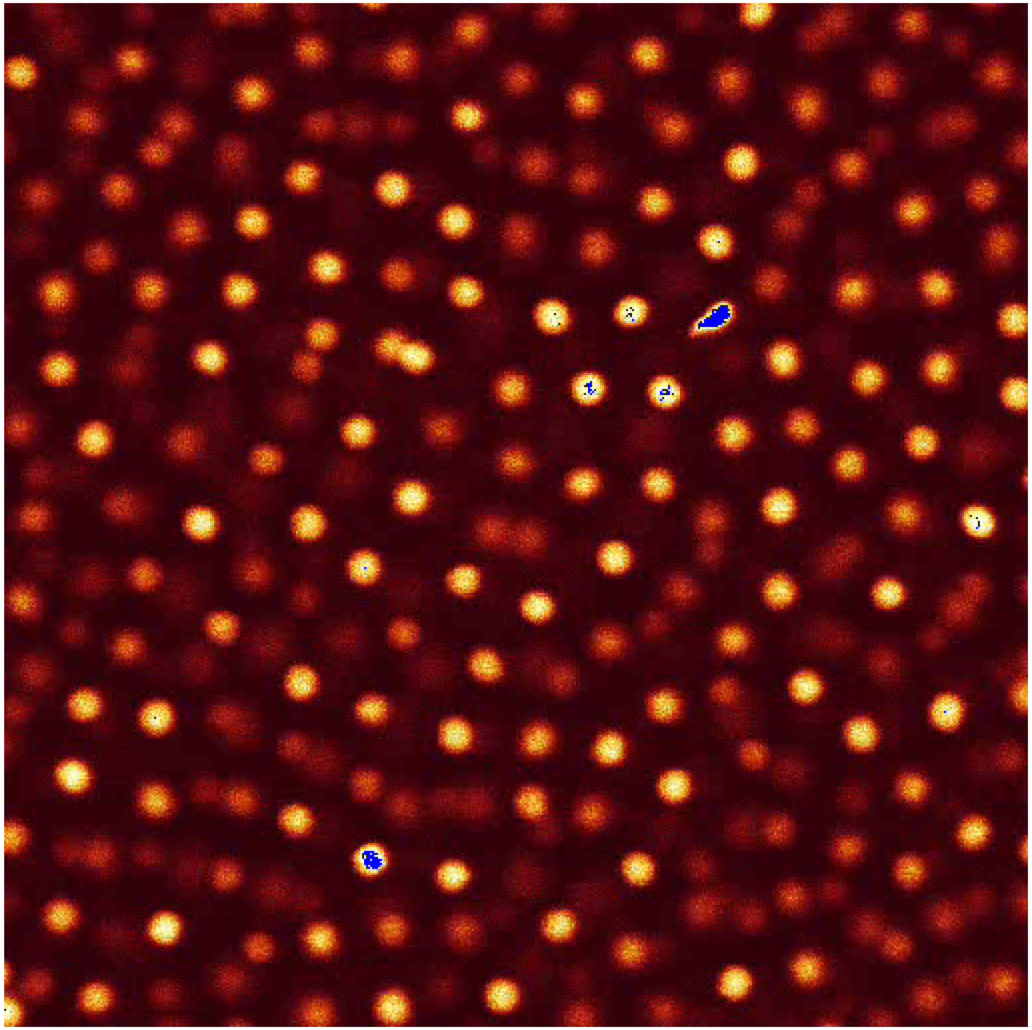
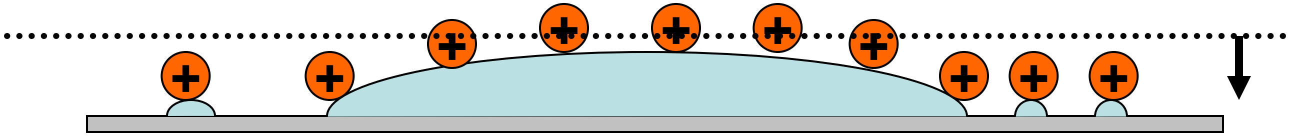
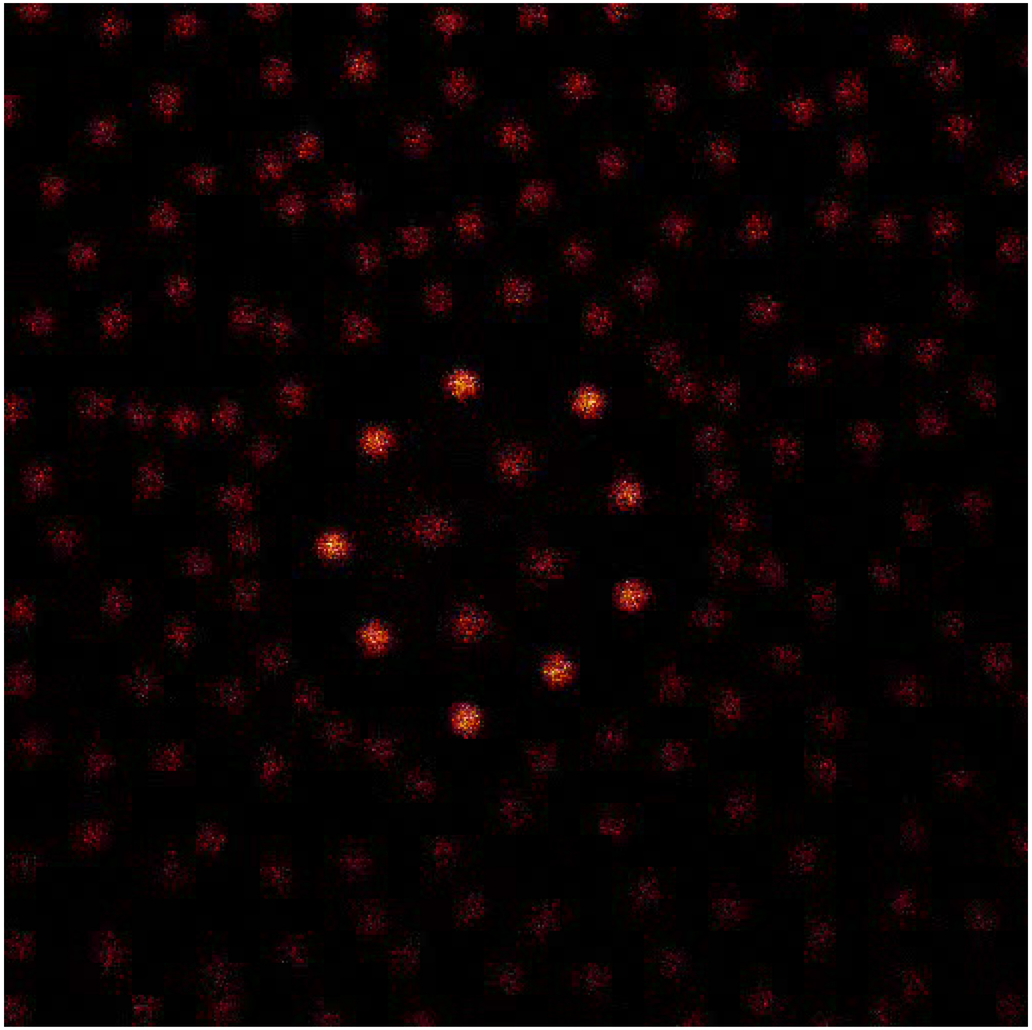


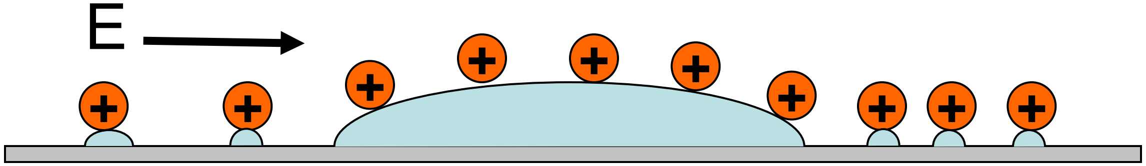
Figure 2.5 The force on a point charge q due to an insulated, conducting sphere of radius a carrying a total charge Q. Positive values mean a repulsion, negative an attraction. The asymptotic dependence of the force has been divided out. $4\pi\epsilon_0 F y^2/q^2$ is plotted versus y/a for $Q/q = -1, 0, 1, 3$. Regardless of the value of Q, the force is always attractive at close distances because of the induced surface charge.

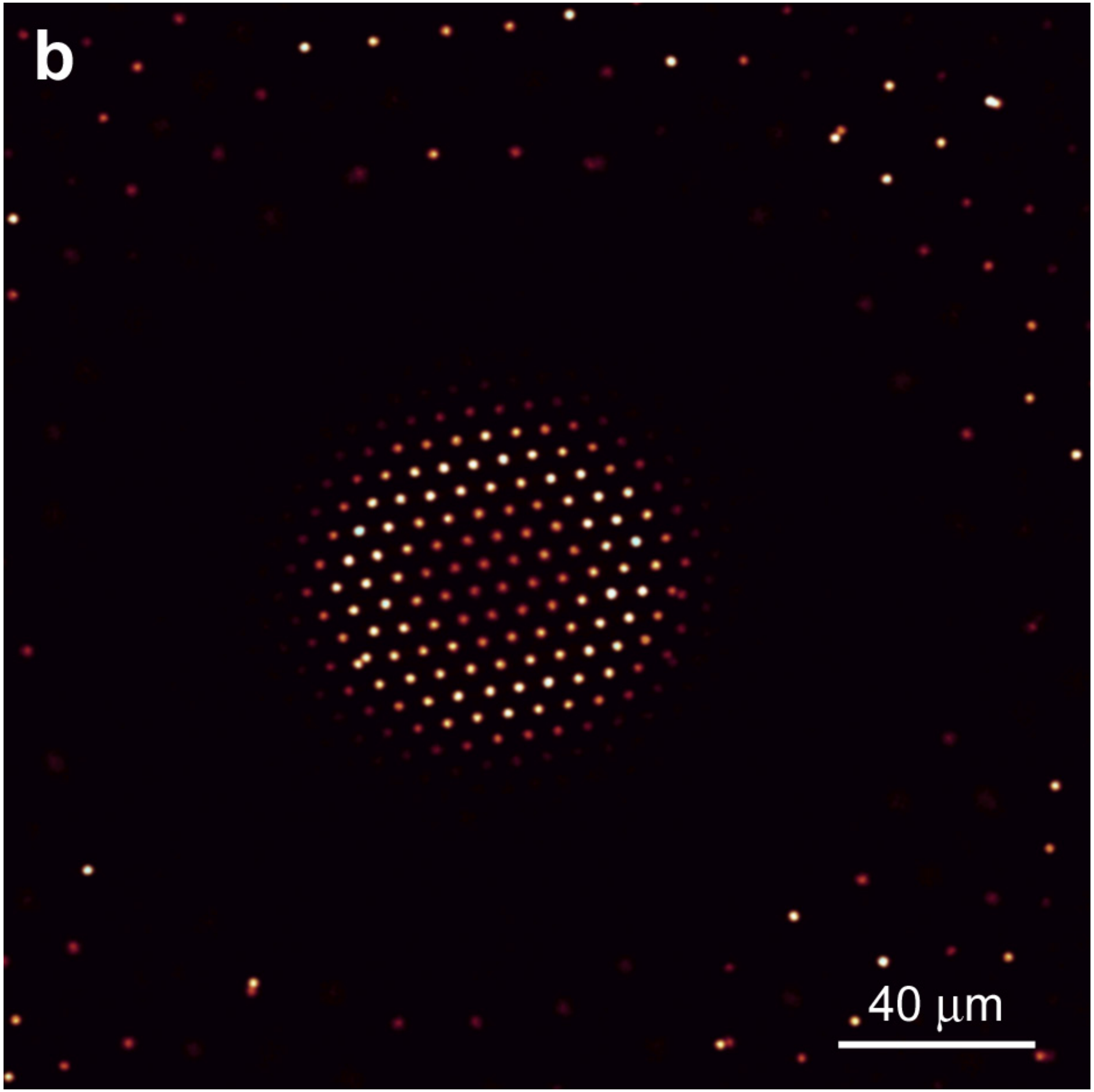




Change Density of 2D Crystal with electric field

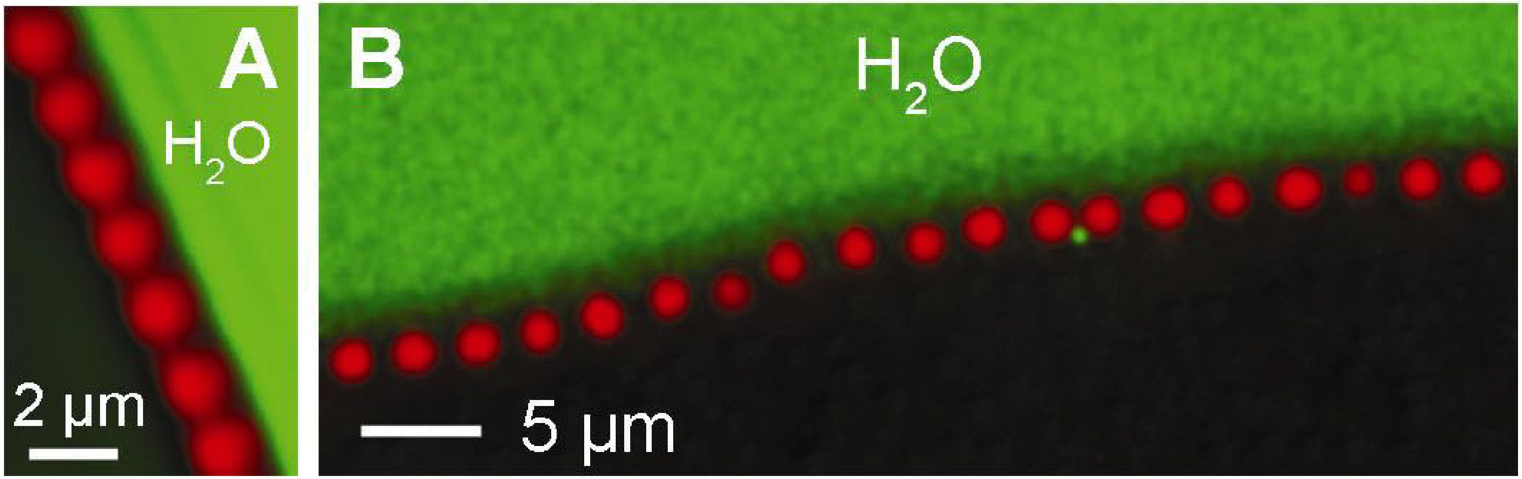




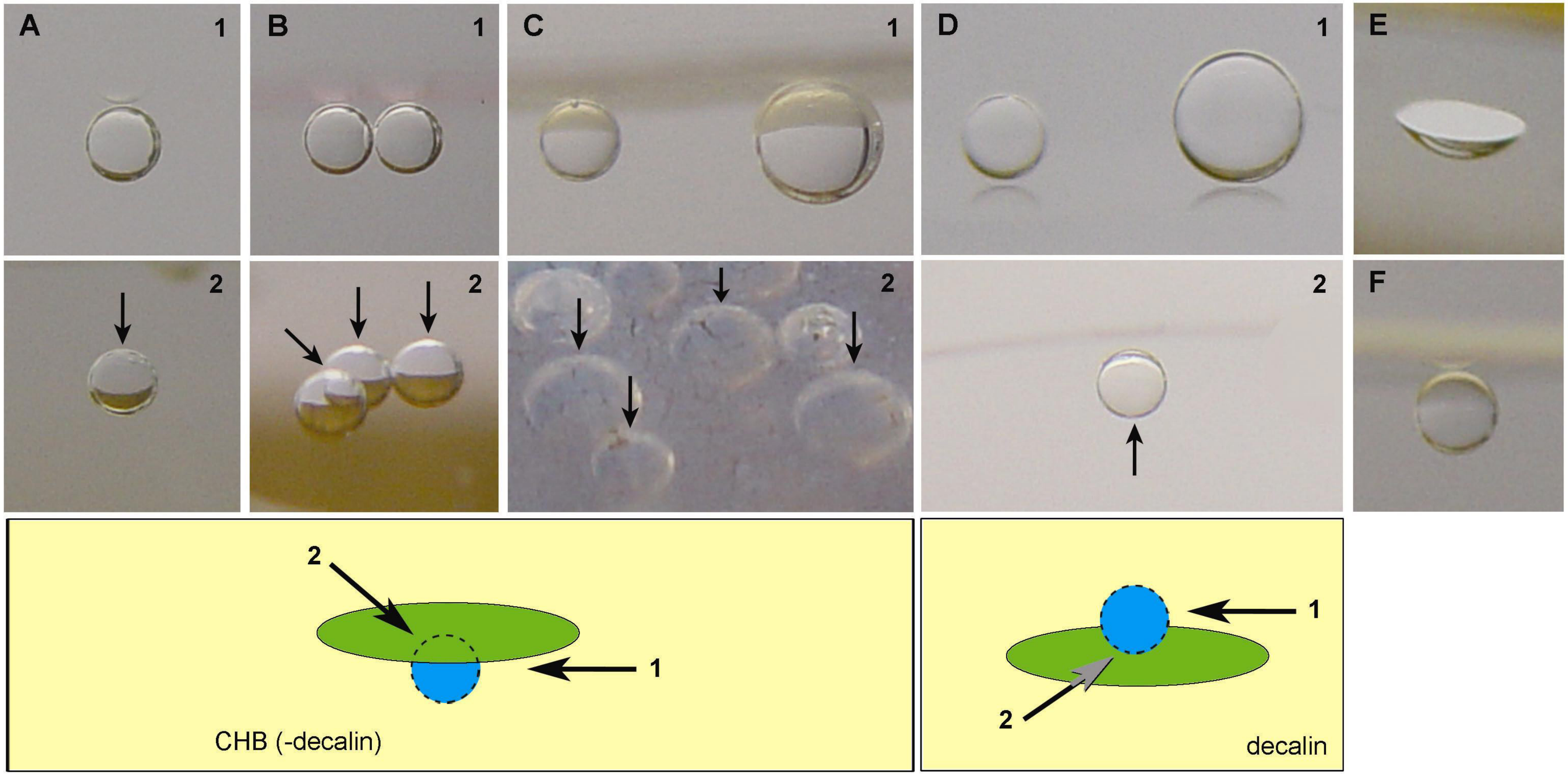


Top-surface of a hemispherical water droplet on the sample cell wall (as seen from the oil phase). Note the depleted zone.

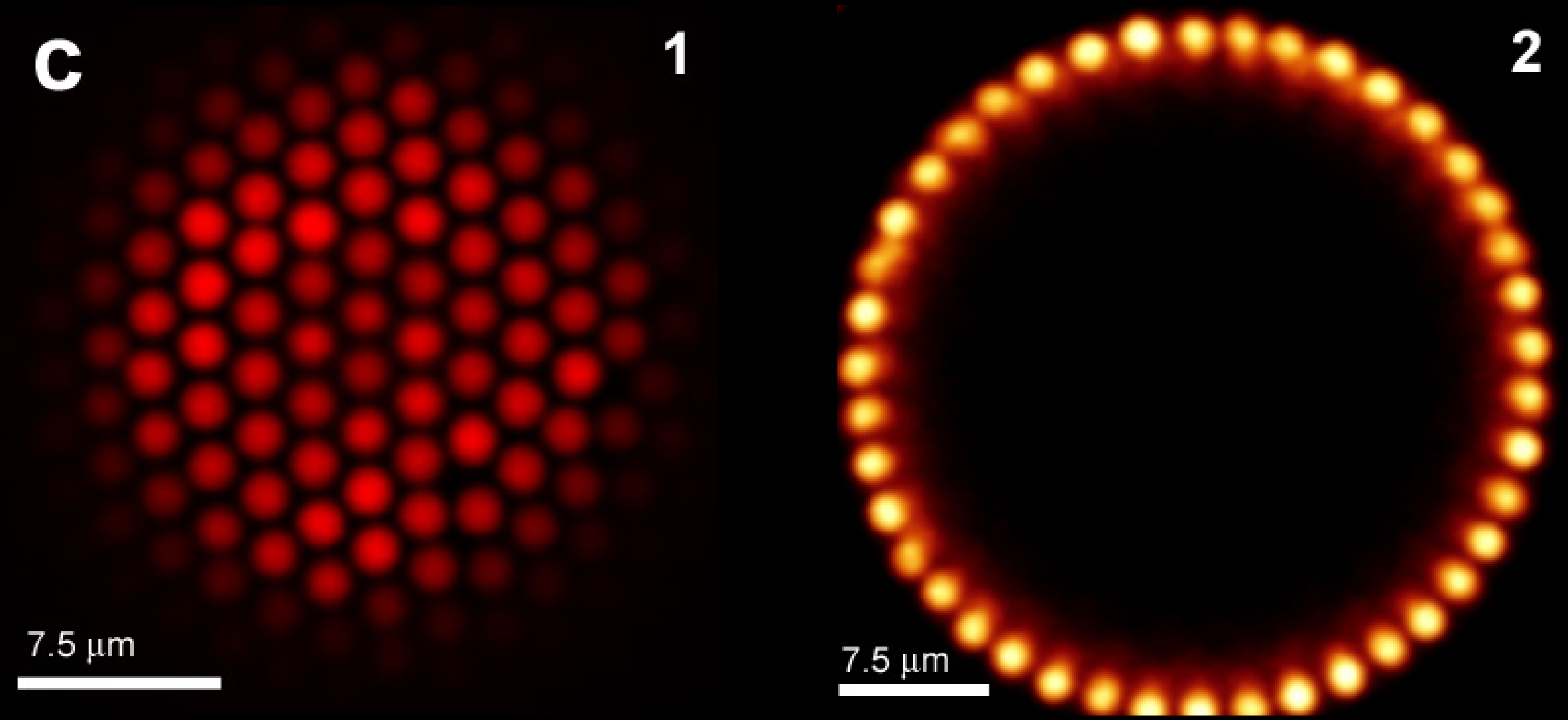
Do PMMA particles wet the interface? – Pickering (particle stabilized) Emulsions?



PMMA-particles (radius 1.08 µm) in CHB-decalin permanently bound at the oil-water interface in various configurations. (**A, B**) Close up images perpendicular to the interface (*15*). The water phase was imaged in bright field transmission mode (green color table) (**A**) or by dissolving fluorescent dye in it (**B**).



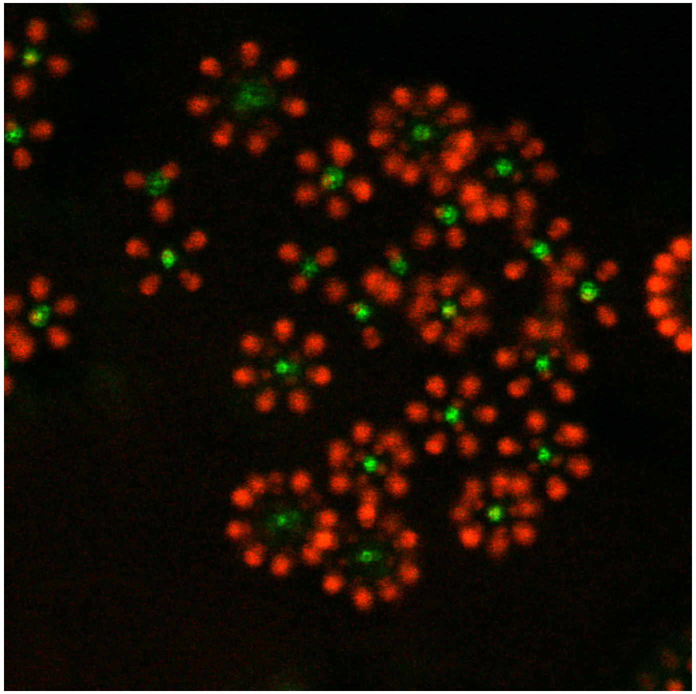
Macroscopic contact angle measurements *(4)*. (**A-C**) Digital photographs of 1-2 mm sized water droplets buoyantly pressing against the bottom side of glass coverslips respectively coated with a homogeneous layer of PHSA-PMMA (deposited from chloroform) and then submerged in CHB-decalin (**A**), coated with fluorescently labelled PMMA particles (radius 1.08 μm) melted together and then submerged in CHB-decalin (**B**), coated with TEFLON® PFA-particles (radius ~90 nm) and then submerged in pure CHB. The schematic drawing indicates the two different directions of viewing: (**1**) perpendicularly from the side or (**2**) under a small angle from the top, through the transparent coverslip. In (**1**) the exact position of the slide can be judged from the droplet's reflection, in (**2**) the arrows indicate the point of contact. All substrates are essentially non-wet. (**D**) Similar experiment with a PMMA-substrate submerged in pure decalin and the water droplets sitting on top of it. The schematic drawing again indicates the different directions of viewing and the arrow in (**2**) indicates the point of contact. For comparison we also show (**E**) a tilted top view of an uncoated glass coverslip, which is clearly wetted and (**F**) a side view of a large solid TEFLON® sheet, which has a contact angle of 180?.



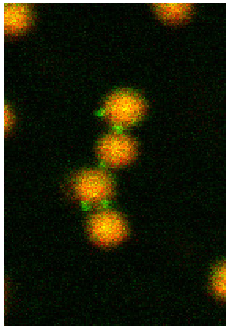
c
1
7.5 µm
2
7.5 µm

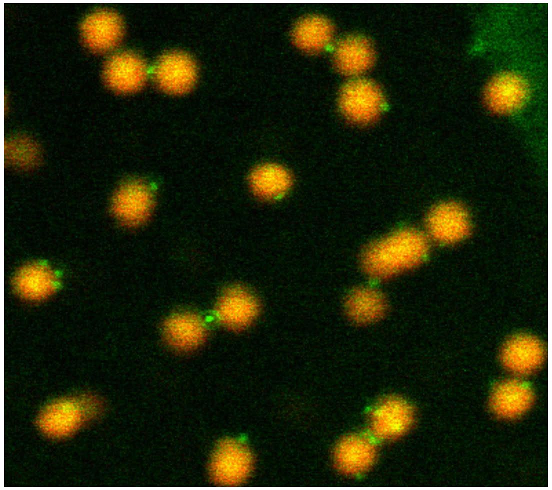
Small water droplets can hold fewer colloids, but always at least two.

RITC-labeled particles in CHB-decalin stirred together with a small amount of FITC labeled water:

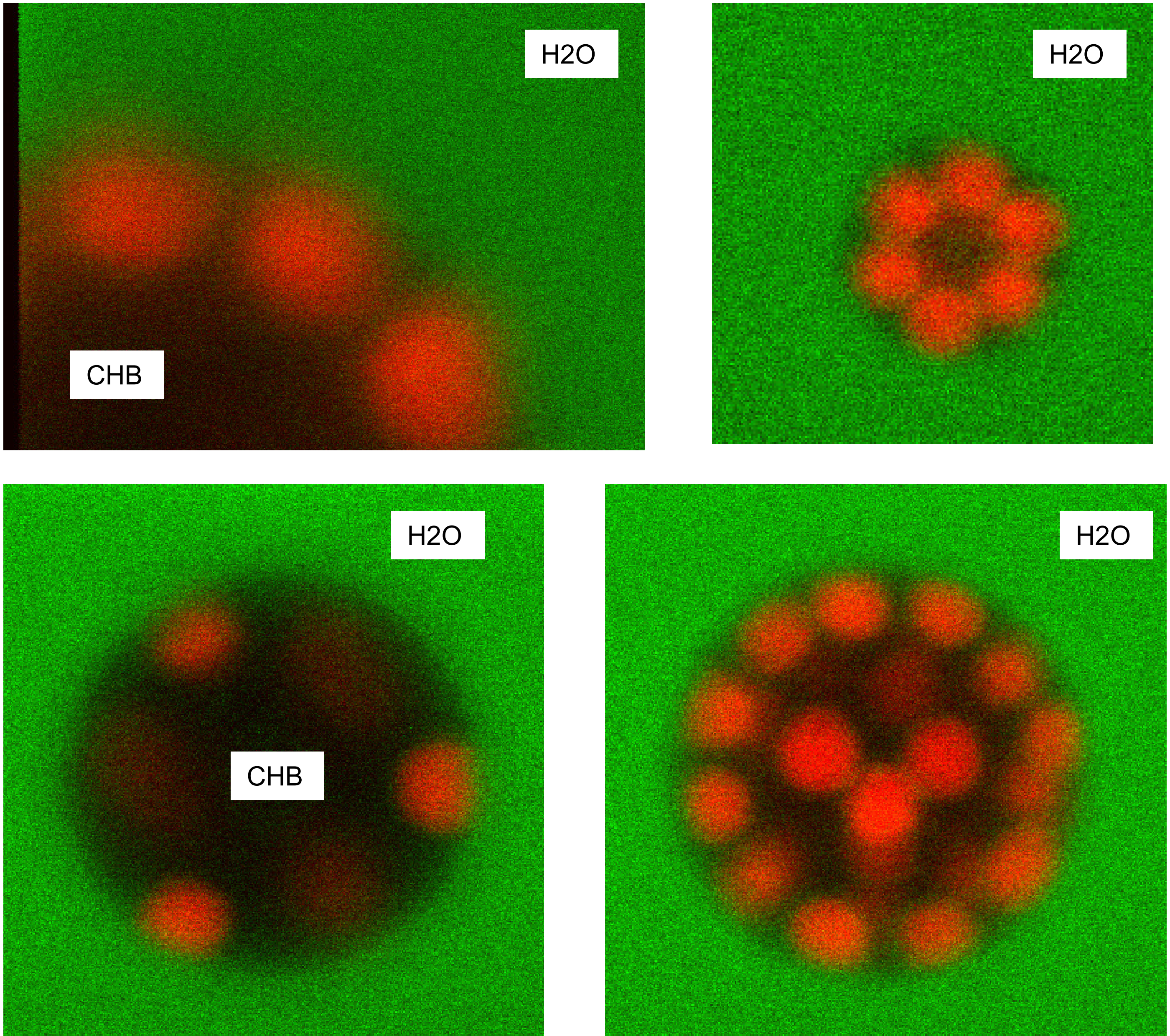


Small droplets can bind particles into clusters: explanation for ‘dense nuclei’?

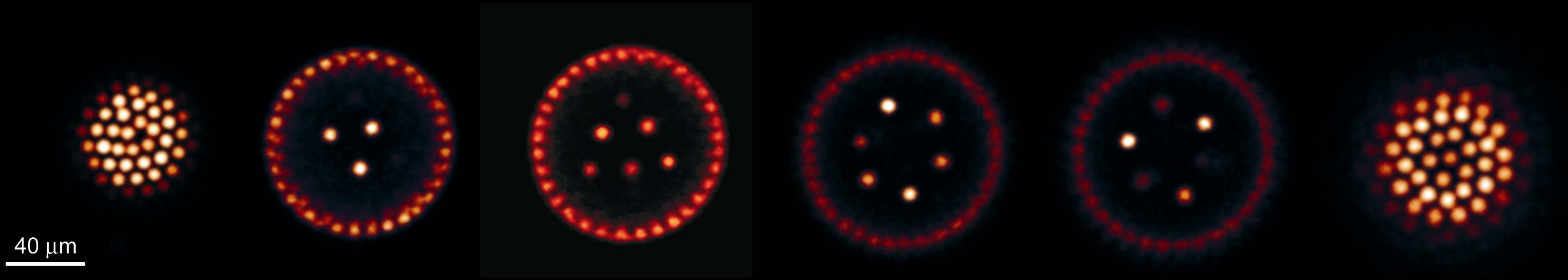




‘Inverse’ colloidosomes of CHB in a water bulk

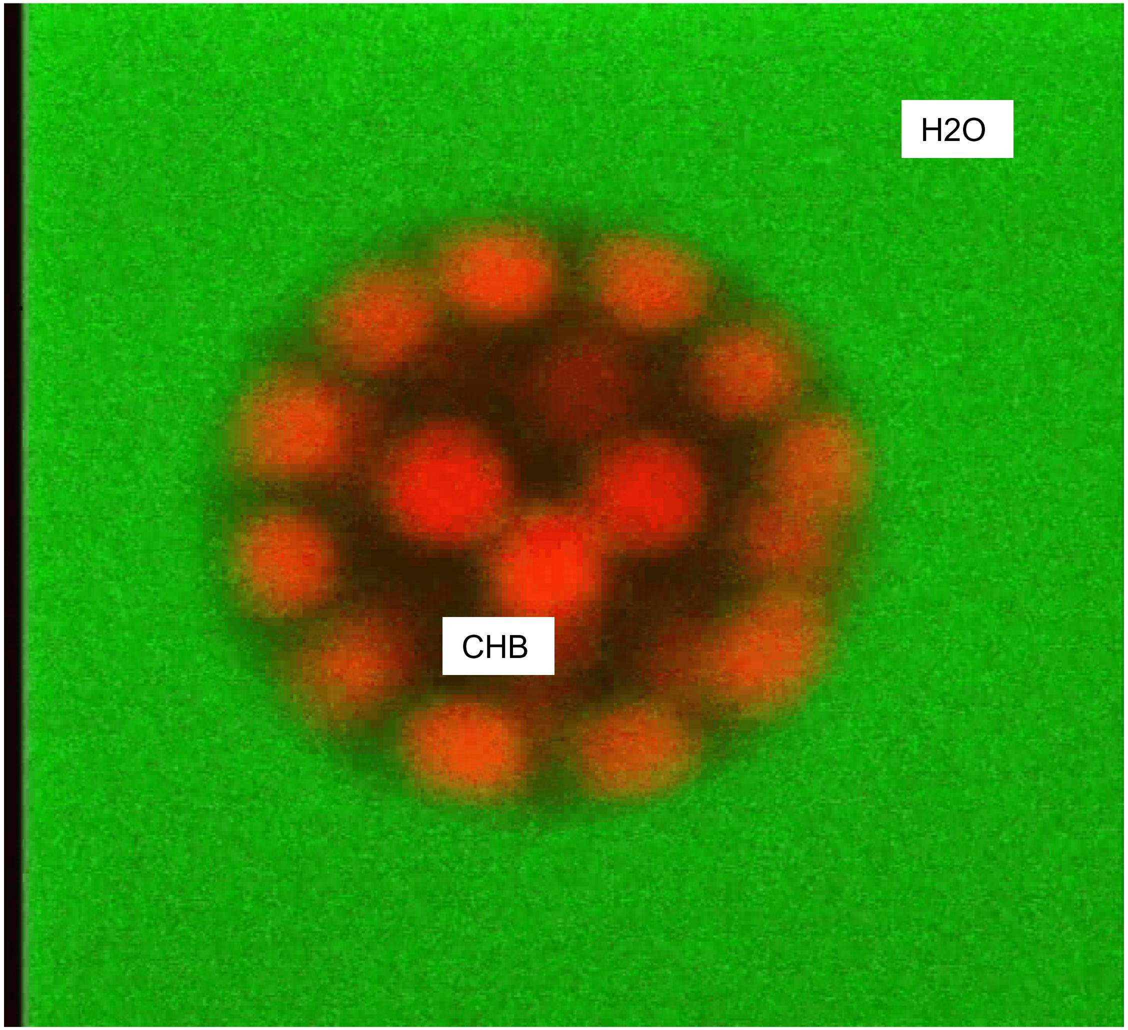


Green = FITC ; Red = RITC



3 Sequence of confocal slices through a particle-containing oil droplet (CHB-decalin) in water. There is a two-dimensional crystal near the inner surface and a freely rotating, three-dimensional Wigner crystal of 12 particles in the interior. Slices 3 and 5 lie halfway between successive particle planes.

3D coulomb crystal in 2D crystal Shell

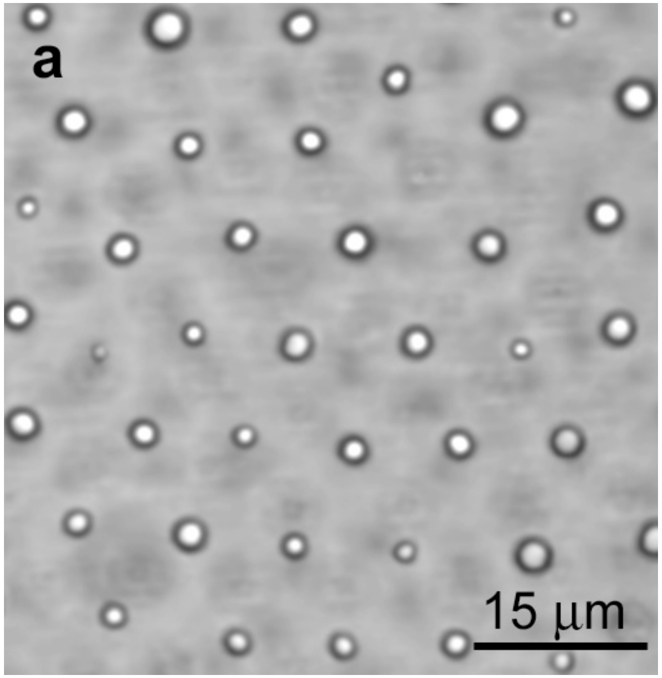


If water Droplets differentially pump ions from oil then we should see charging effects without colloids present

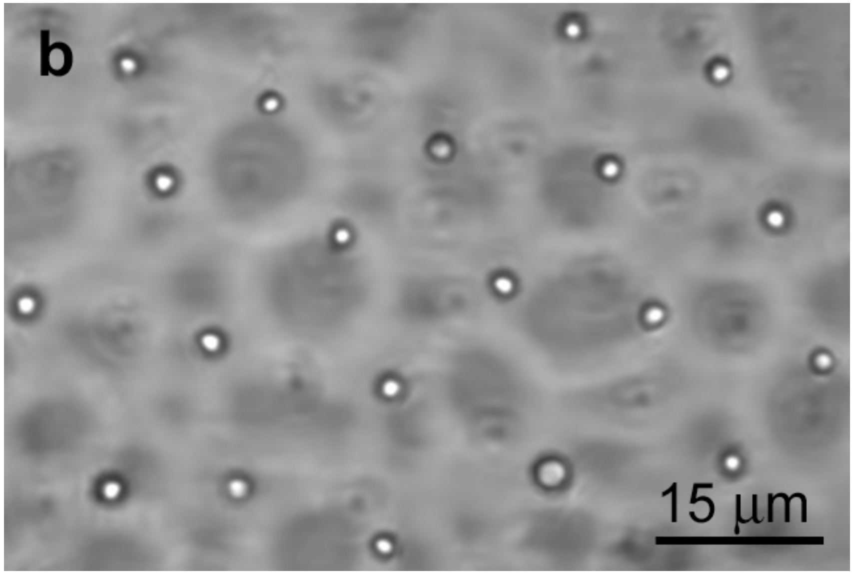
Two samples of clean cc CHB/decalin, with a drop of water added and sonicated:

- Wigner Crystal of 2-3 micron water droplets
- Emulsion stabilized by charge alone – no surfactants
- Shake instead of sonicate, big, polydisperse, charge stabilized emulsion

New form of crystallized water
- Ice 10?

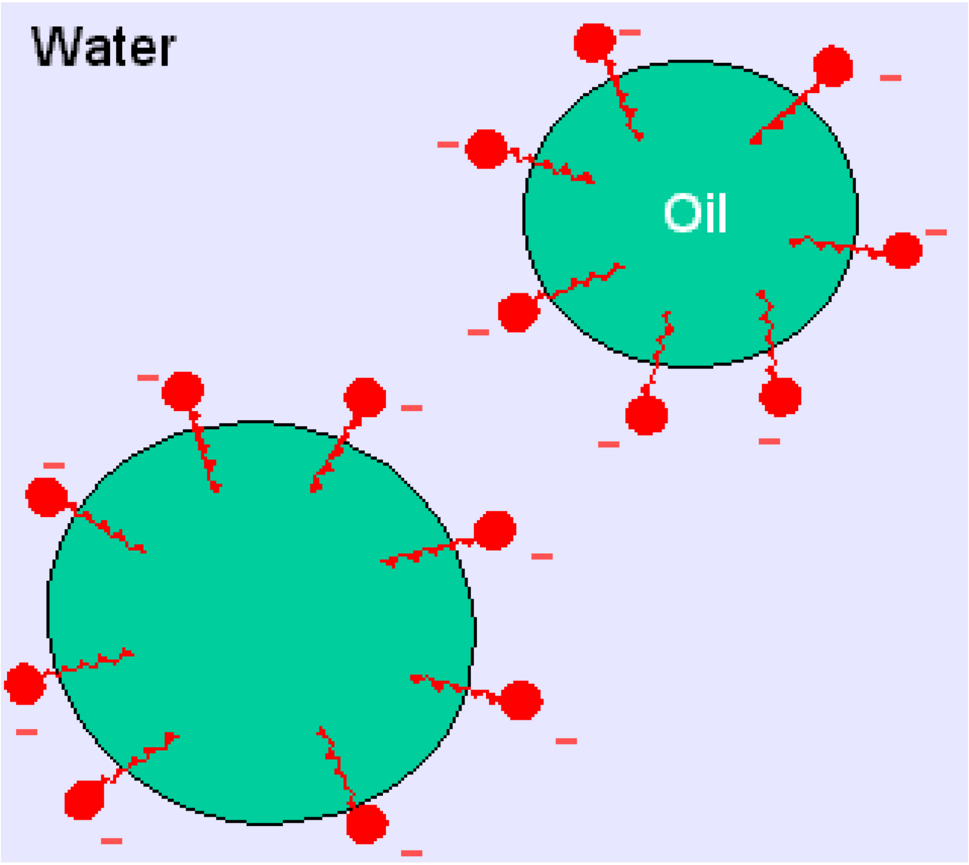


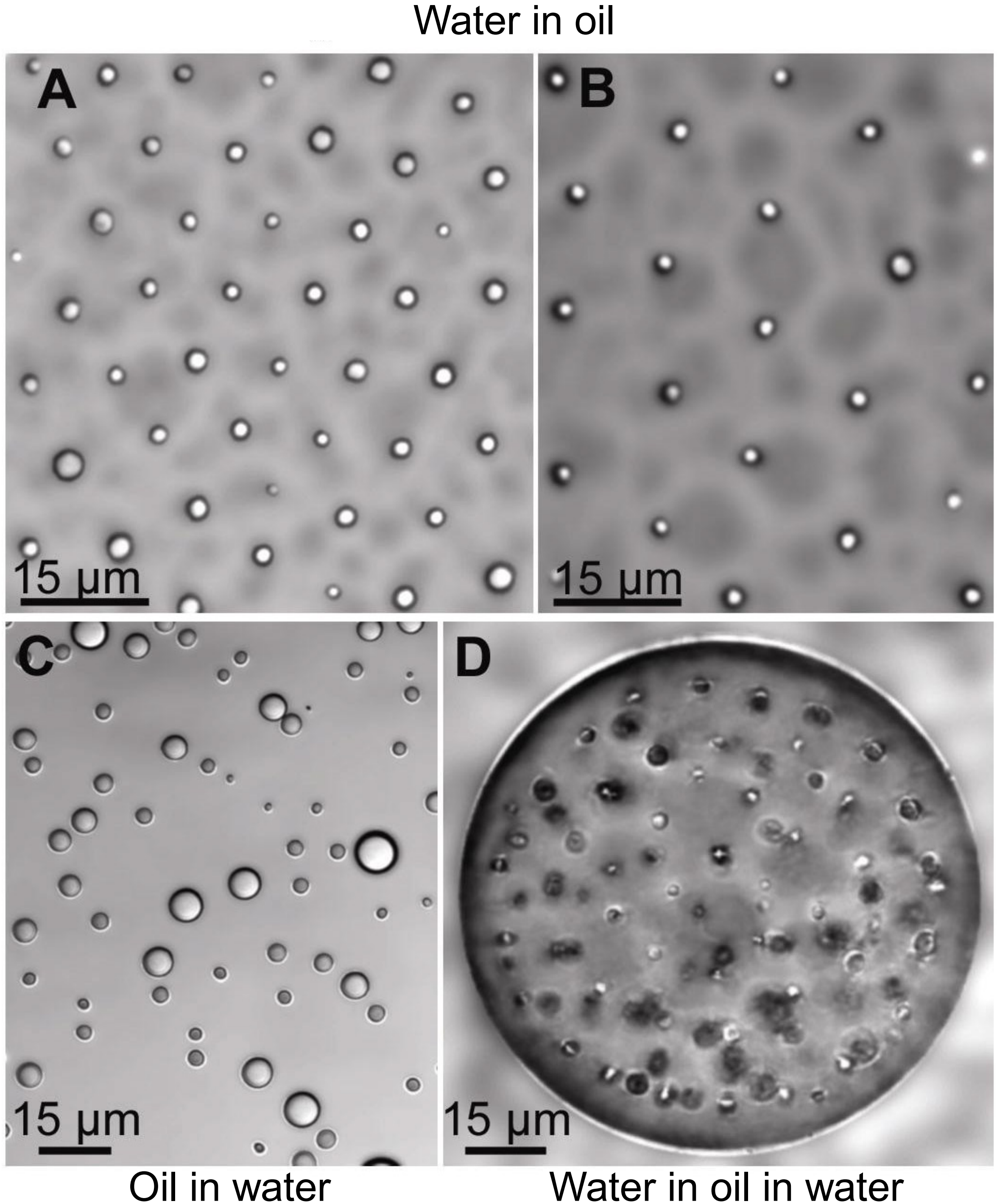
H2O - CHB



H2O – CHB/decalin

Usually you need a surfactant to stabilize an emulsion





Bright field transmission images of charge-stabilized, additive-free emulsions.

(A) Water droplets in CHB

(B) CHB-decalin after 2 minutes of sonication, near the top-wall of the sample cell.

(**C**) CHB droplets in water, near the bottom of the sample cell.

(**D**) Wigner crystal of small water droplets inside a bigger CHB-droplet (in water). Note that curvature effects distort the image and that some droplets are not in focus.

Solvents tried for the preparation of additive-free, charge-stabilized, crystal forming water-in-oil emulsions.

Solvent	Dielectric constant*	Stable, crystal forming droplets ?
dodecane	2.0	no
cyclohexane	2.0	no
bromoform	4.3	yes
chloroform	4.7	yes
dichloromethane	8.9	yes
1-butanol	17.3	no
cis-decalin	2.2	no
decalin-CHB 30% (by weight)	3.5	no
decalin-CHB 50%	4.5	repulsive droplets, but no crystal
decalin-CHB 75%	6.0	yes
cyclohexyl bromide (CHB)	7.9	yes

* Exact value only known for the pure solvents. For the mixtures it was estimated based on the partial volumes of the components.

Other systems that form stable surfactant free ordered emulsions so far:

Hydrophillic	Hydrophobic
Water	dichloromethane (ε~8.9)
Glycerol	CHB (ε~7.9)
	chloroform (ε~4.7)
	bromoform (ε~4.3).

1-butanol (ε ~ 17.3)
doesn't work

the interesting range is approximately 4 < ε < 10

Who's to Blame

Mirjam Leunissen, Alfons van Blaaderen

Debye Institute, Univ. Utrecht

Bill Russel

Princeton - Chem Eng.

Matt Sullivan Bob Austin

Weining Man Kun Zhao

Princeton - Physics

Andrew Hollingsworth PC

Center for Soft Condensed Matter Research

NYU - Physics.

Kun Zhao
Matt Sullivan
Bill Russel
Marie-Pierre Valignant
Weining Man
Mirjam Leunissen
Andy Hollingsworth

Summary

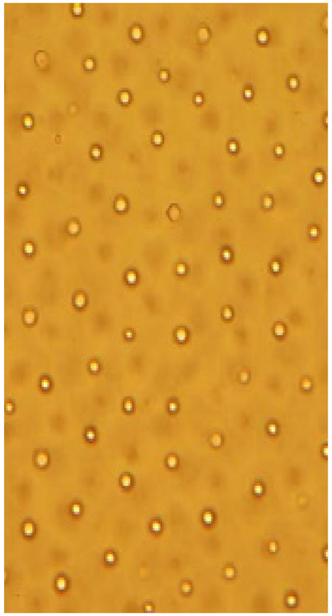
Classical aspects of Electrostatic Crystals are readily studied in Colloids and Emulsions

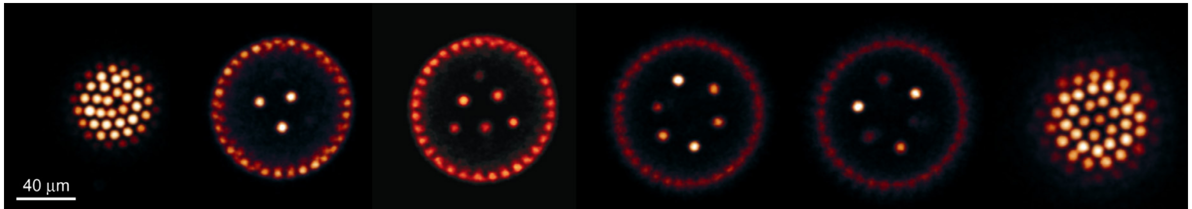
Advantages:
Control charge, screening, distance….
Real space observation (much better than k space) with microscopy
Slow, dynamics happens in real time
Connections to chemistry, processing, biology

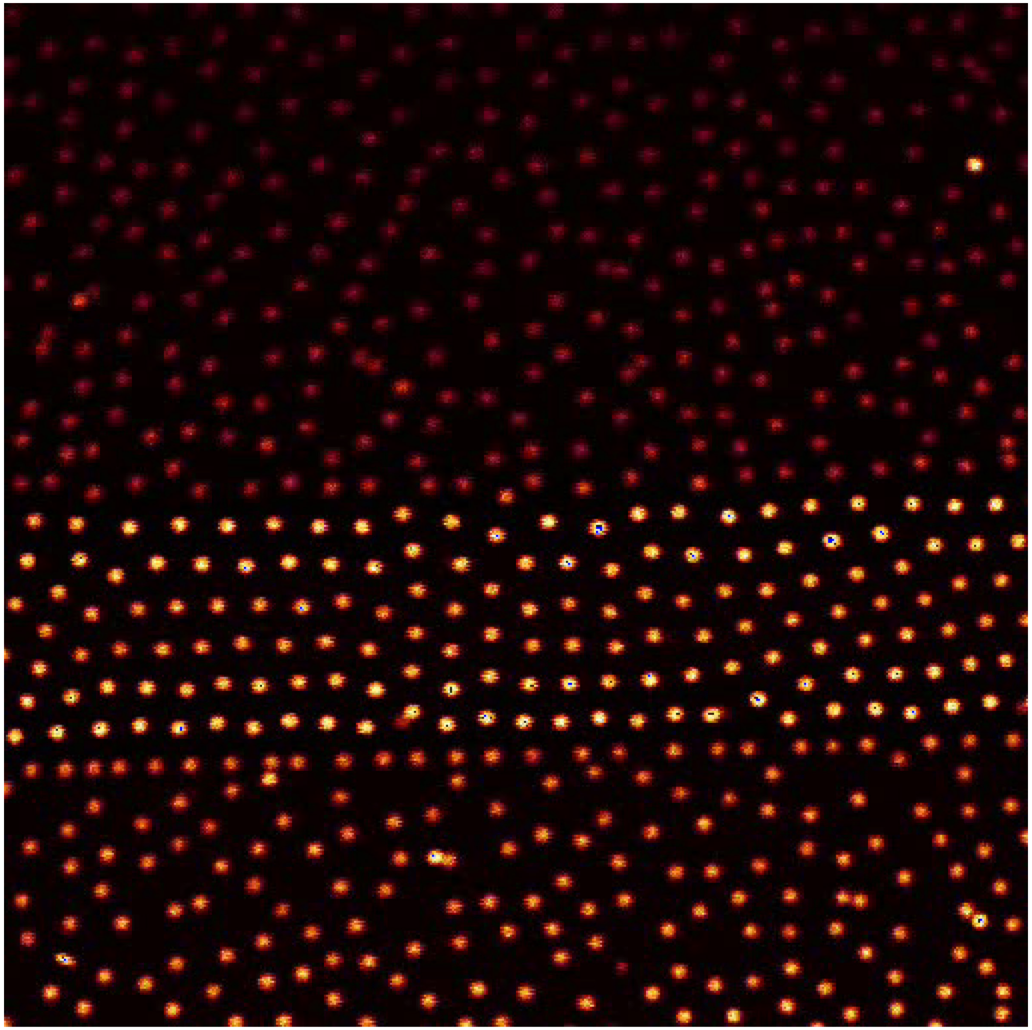
Disadvantages:
Not quantum
Overdamped a lot.

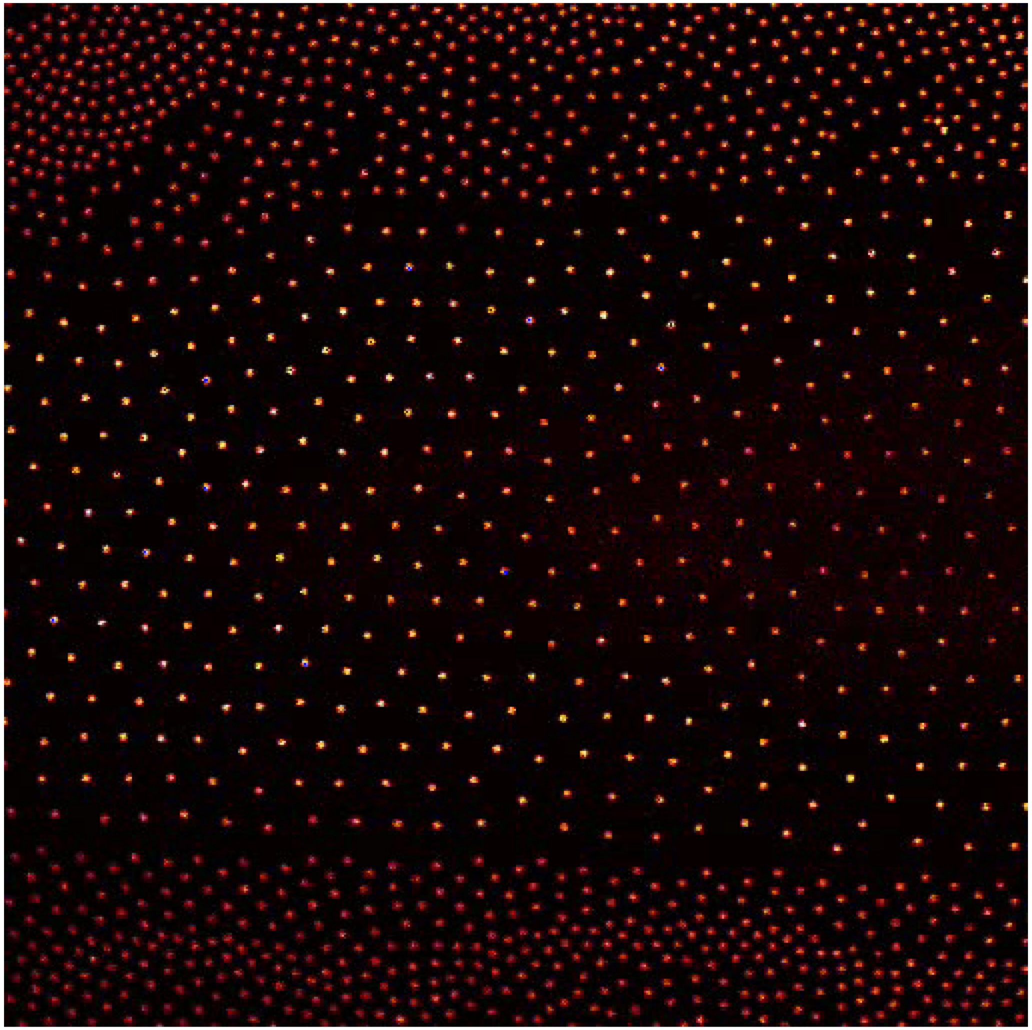
Today's Main message: Water sucks (ions out of oil)
•Leaves almost unscreened interactions
•self charges
•Provides conductor for image charge 2D crystals

(ε ~ 6.0)









History

1957	Williams + Smith	Tipula Iridescent Virus
1959	Klug, Franklin et al.	Structure
1968	Woods et al.	Polystyrene Spheres
1969	Hiltner + Krieger	Bragg Scattering
1974 76	Williams + Crandall + Wojtowicz	Structure, Melting
1974	Kose, Hachisu et al.	Bragg Scattering
1975	Schaefer + Ackerson	Dynamic Light scattering
1977	Mitaku et al.	Shear properties with ultrasound
1978	Pieranski et al	Dislocations, Shear Mod. 2-dim.
1979	Clark et al.	Shear melting