COLLOIDAL PARTICLES AS EMULSION AND FOAM STABILISERS

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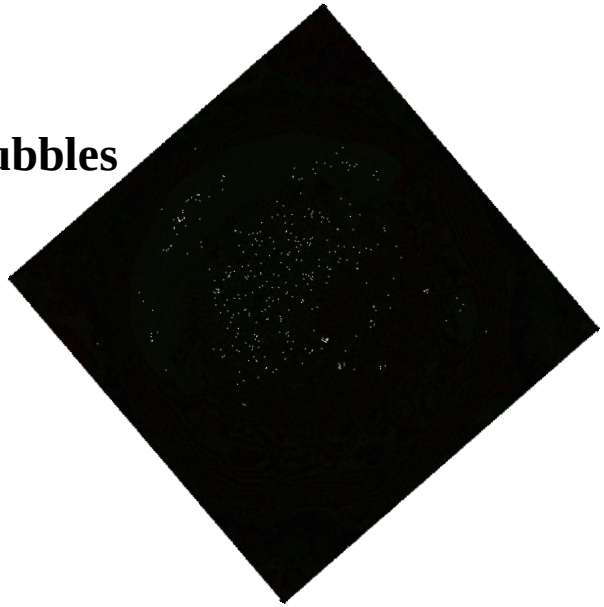
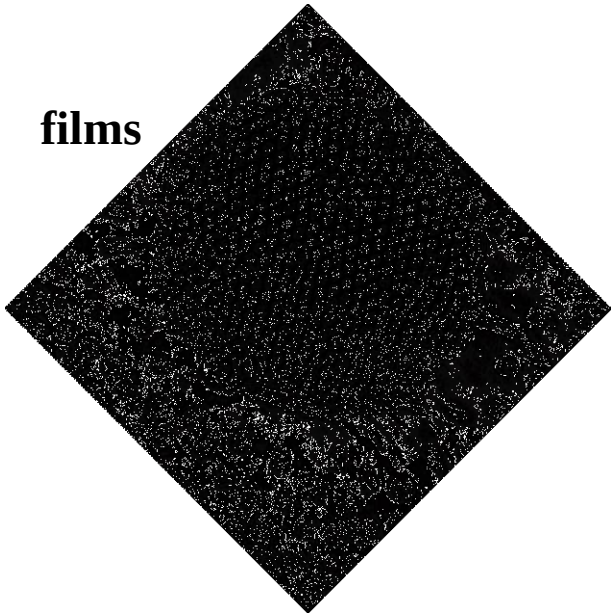
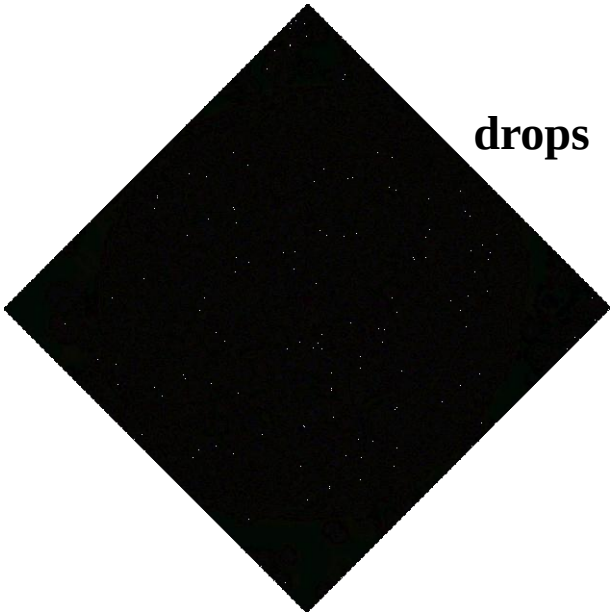
bubbles



films



drops



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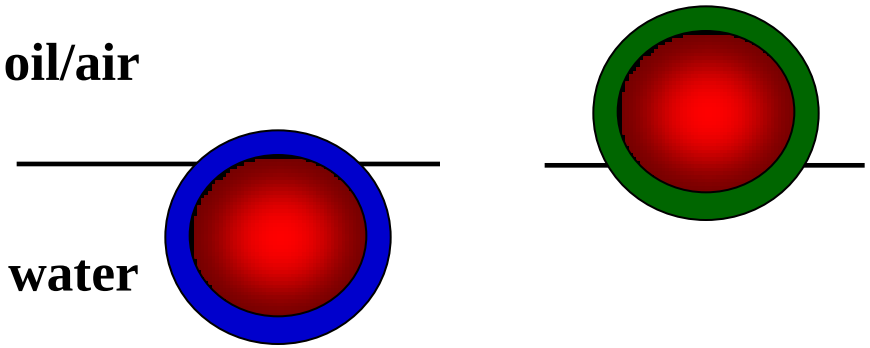
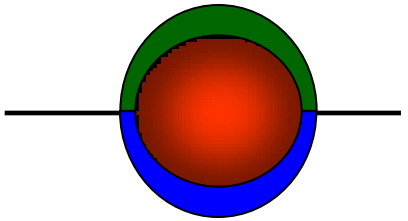
COLLOIDAL PARTICLES: nm - μm

Particles may be surface-active but not amphiphilic

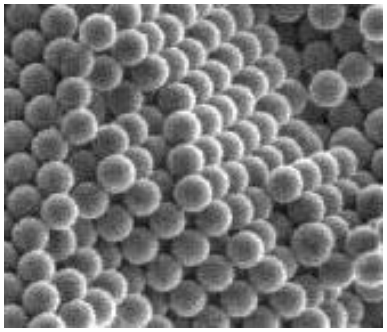
Exception:

Janus particles





HYDROPHILIC



silica

clay (disk)

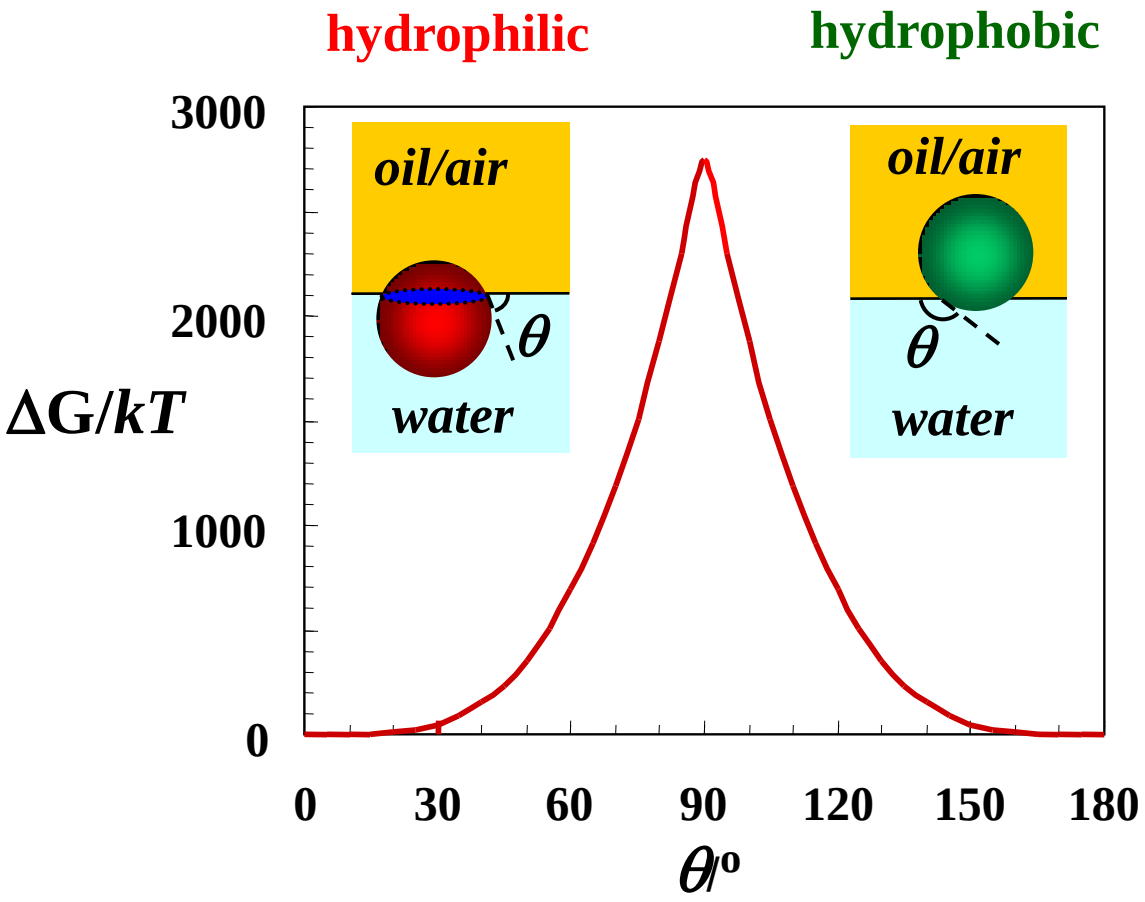
HYDROPHOBIC

polymer latex

carbon

ADSORPTION OF PARTICLES AT FLUID INTERFACES

Free energy gain by losing an area of fluid-fluid interface



$$\Delta G = \pi r^2 \gamma (1 \pm \cos\theta)^2$$

r = 10 nm,

γ = 36 mN m^{-1}

Particles strongly held at interfaces: irreversibly adsorbed

Contact angle is particle equivalent of surfactant HLB number

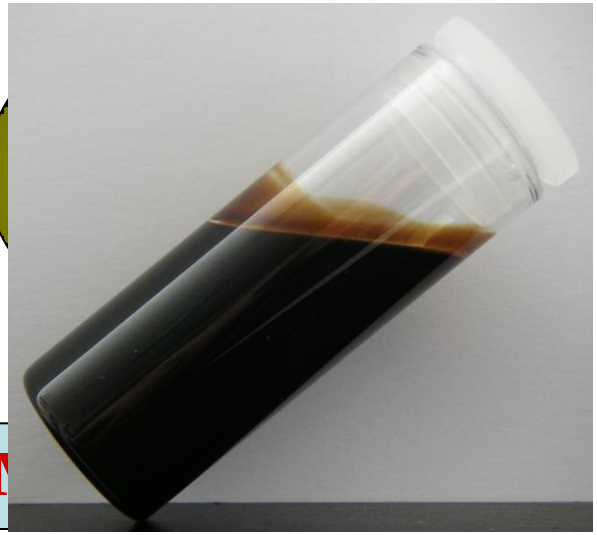
cleaning of apples

mayonnaise

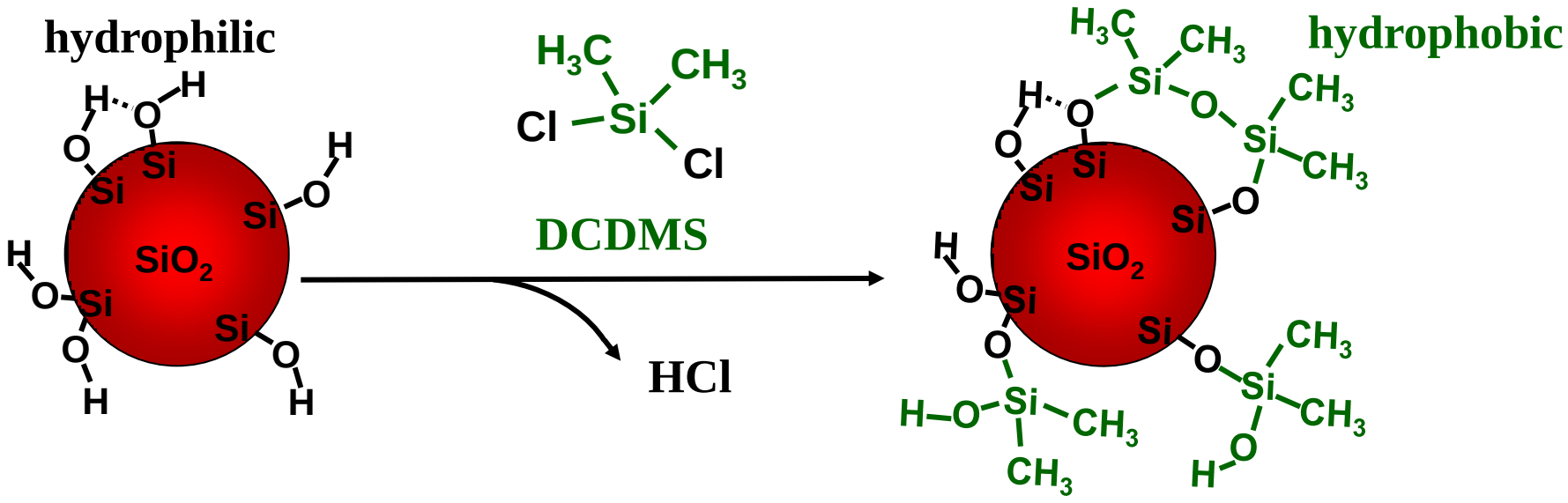
SOLID PARTICLES AT LIQUID INTERFACES

flotation of ores

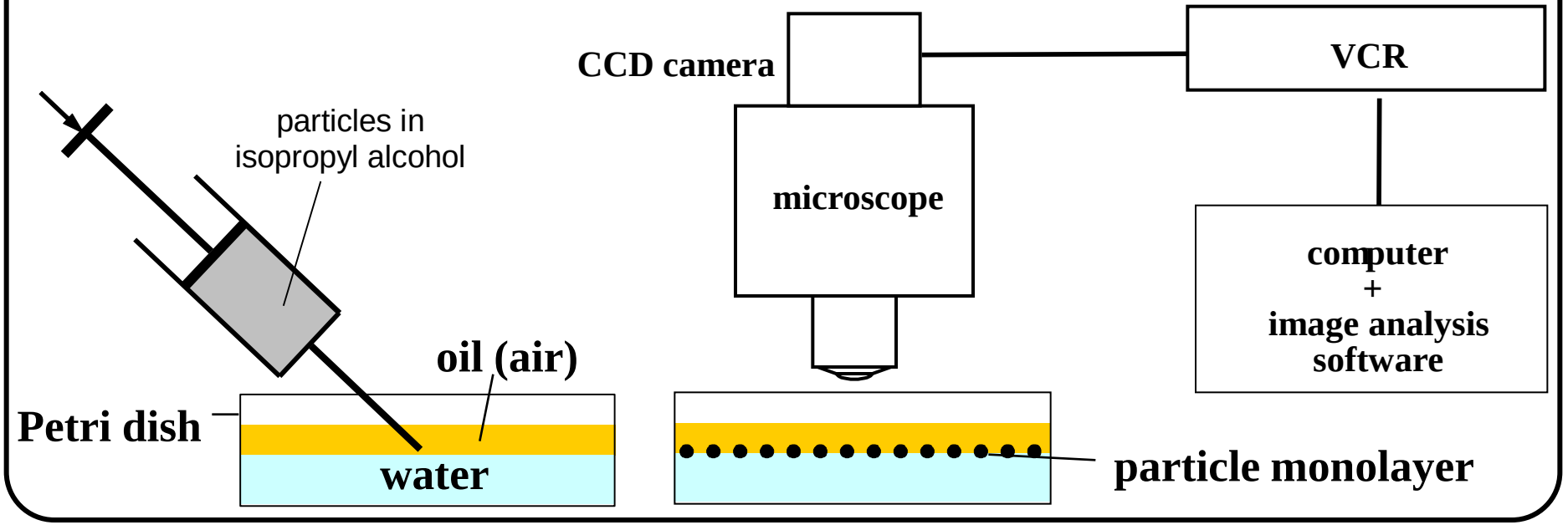
crude oil



Surface modification of silica particles



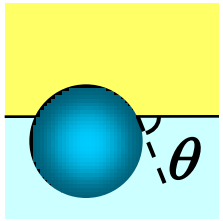
Formation of planar monolayers



Planar Monolayers

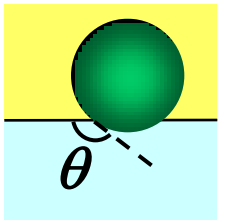
1 μm monodisperse silica particles

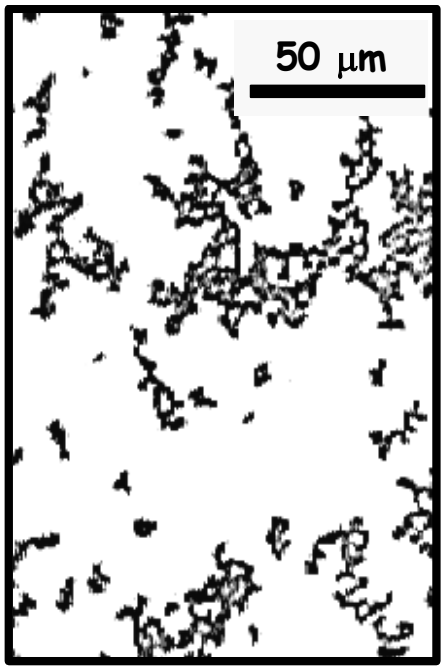
octane-water interface



disordered monolayers

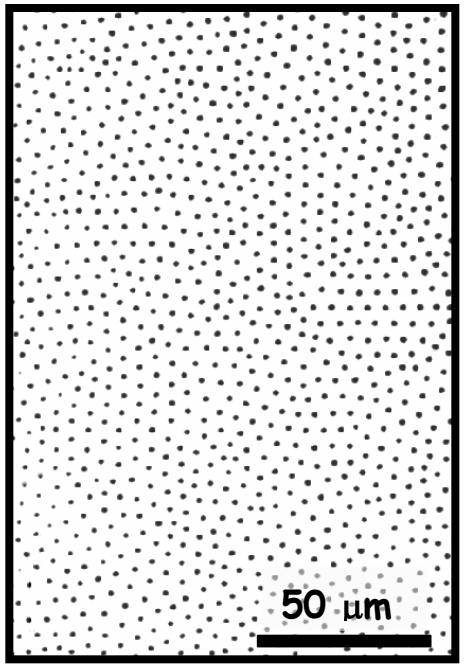
ordered monolayers



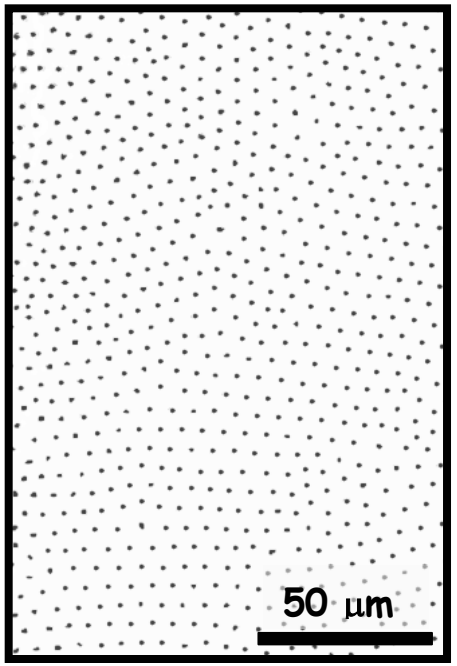


$\theta = 70^{o}$

$\theta = 115^{o}$



$\theta = 129^{o}$

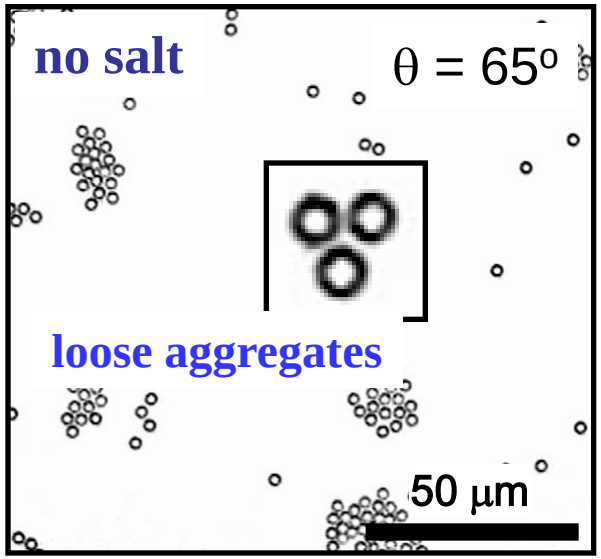


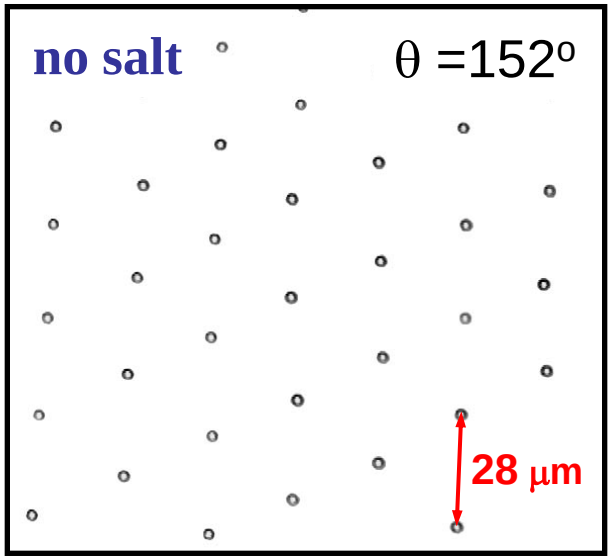
$\theta = 150^{o}$

Planar Monolayers

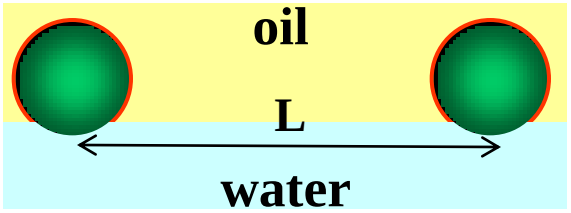
3 μm silica particles at octane-water

hydrophilic pH = 5.7 hydrophobic



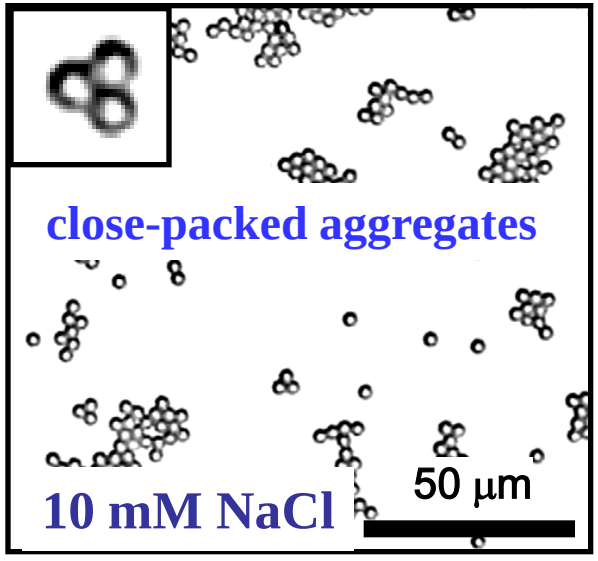


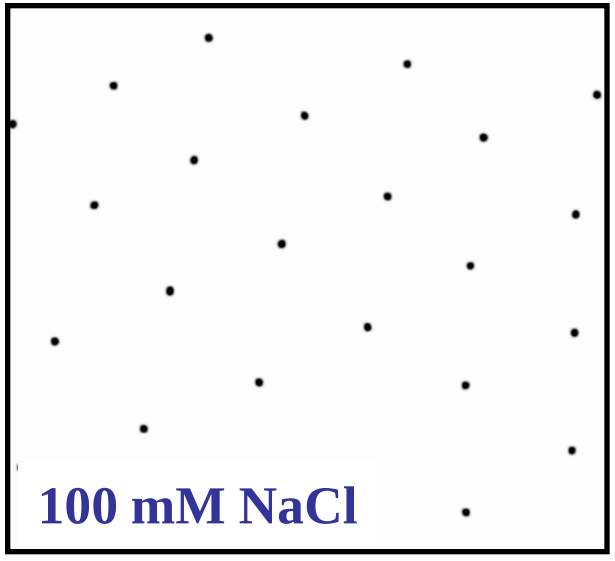
due to charges at particle-oil surface?



repulsion through water

long-range repulsion through oil





Optical tweezers:

Coulombic repulsive force $\propto L^{-4}$

Spencer U. Pickering, M.A., FRS (1858-1920)

Professor of Chemistry, Bedford College

Director of Woburn Experimental Fruit Farm

$CuSO_4$ (insecticide) + CaO (lime) → ppt. basic $CuSO_4$

superior emulsifier to soap; "*pellicle around globules*"

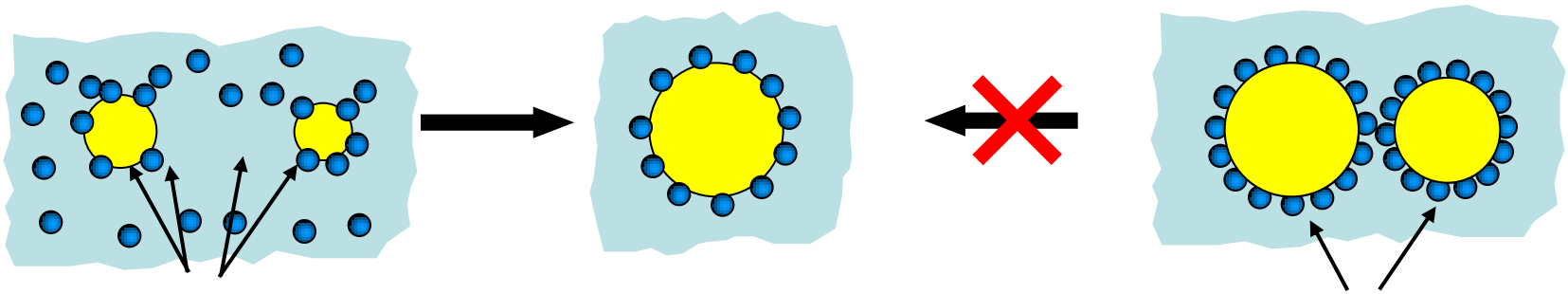
J. Chem. Soc., **91**, 2001 (1907)

CXCVI - Emulsions

"…the subject had already been investigated by Walter Ramsden, but his work, unfortunately, did not come under the notice of the writer until that here described had been completed."

Proc. Roy. Soc., **72,** 156 (1903)

Particle-Stabilised Emulsions Limited coalescence



dilute particle monolayers

interfacial area decreases

monolayer density increases

dense particle monolayers

a steric barrier against coalescence

w/o

1 cm

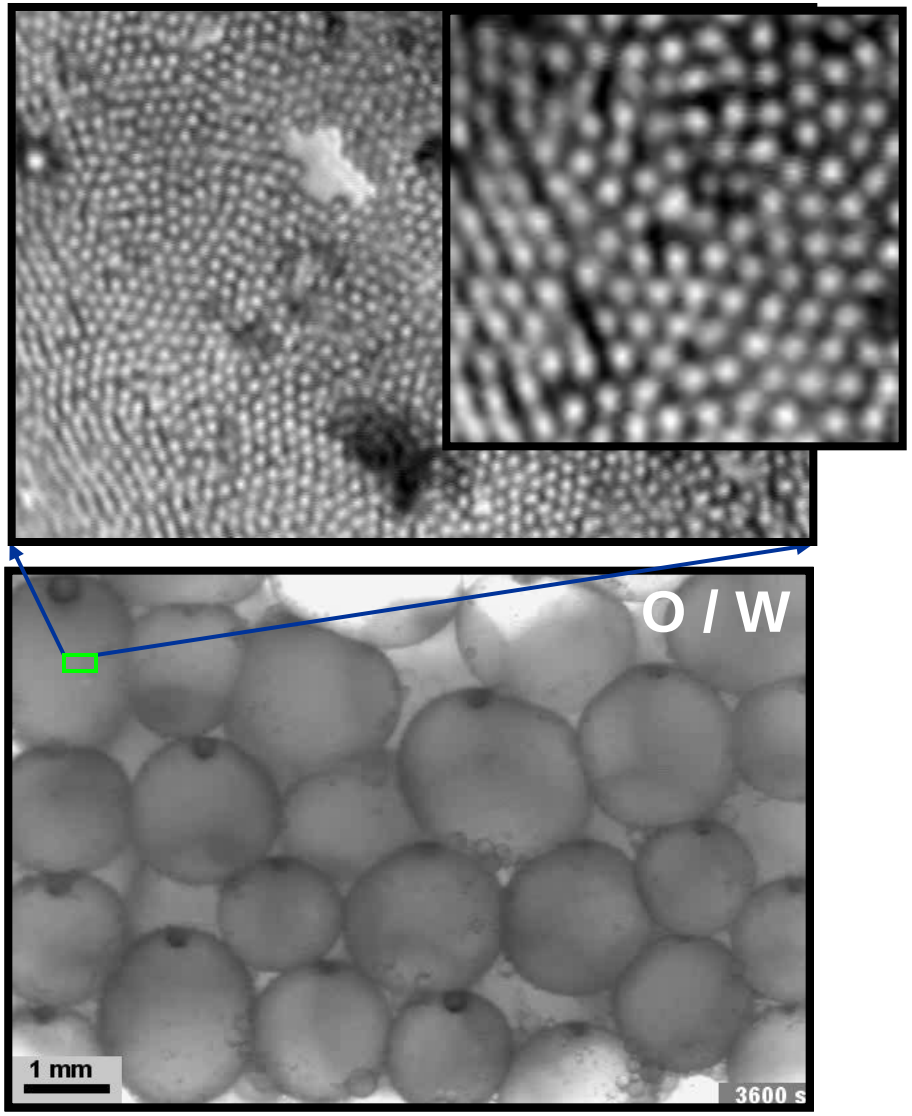
What is the limiting monolayer density needed to prevent coalescence?

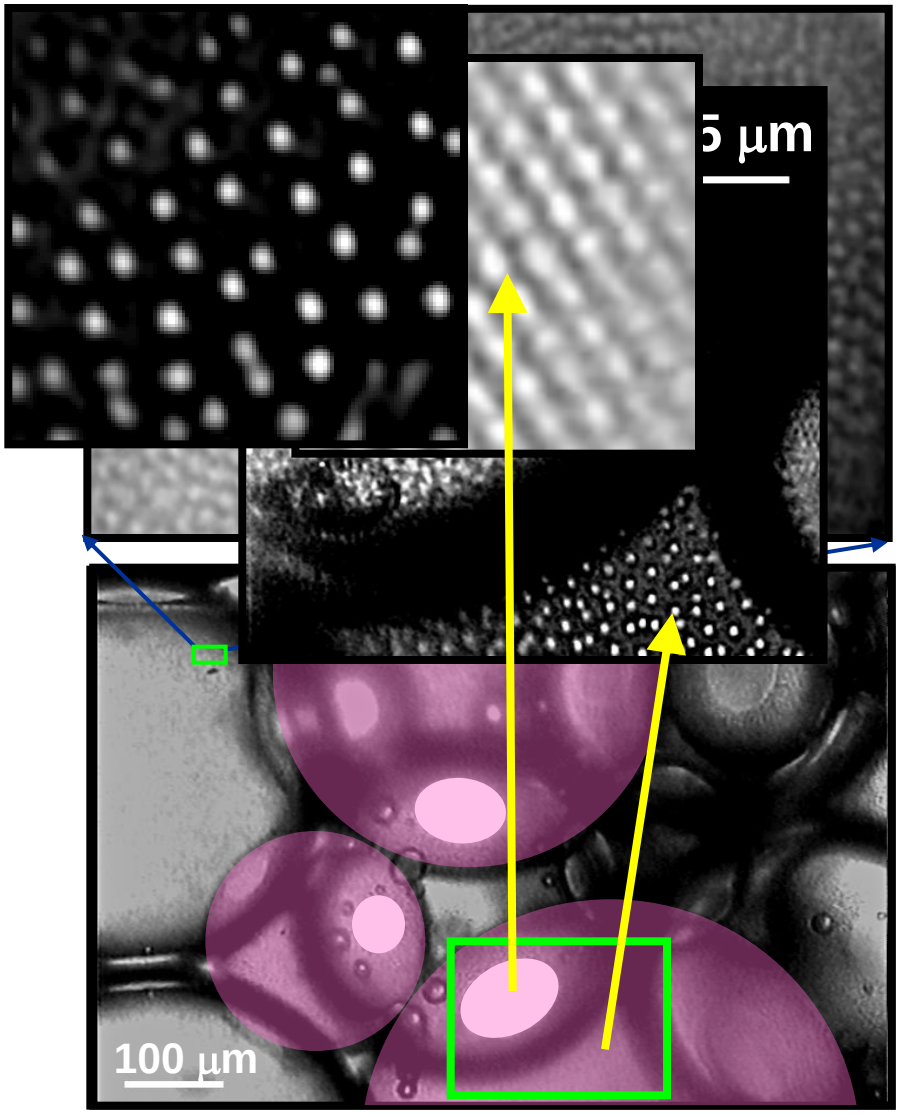
Does it depend on particle hydrophobicity?

Simple Emulsions 3 μm silica particles; 1 wt.% in emulsion; octane:water = 1:1

hydrophilic particles $\theta = 65^{o}$

hydrophobic particles $\theta = 152^{o}$

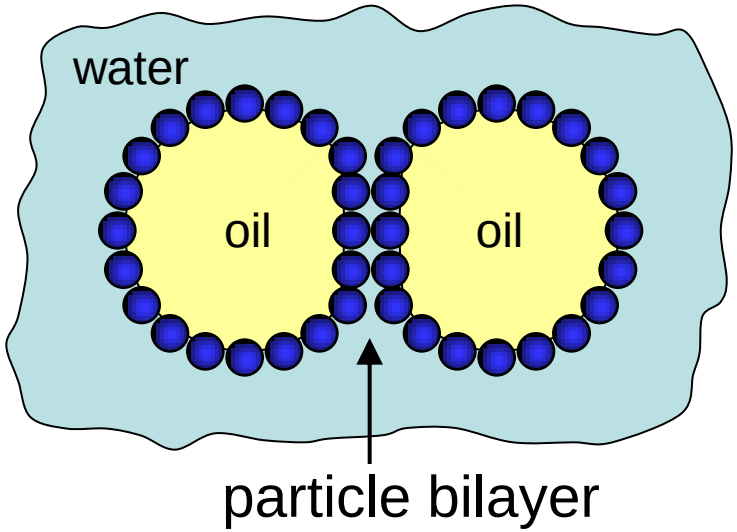




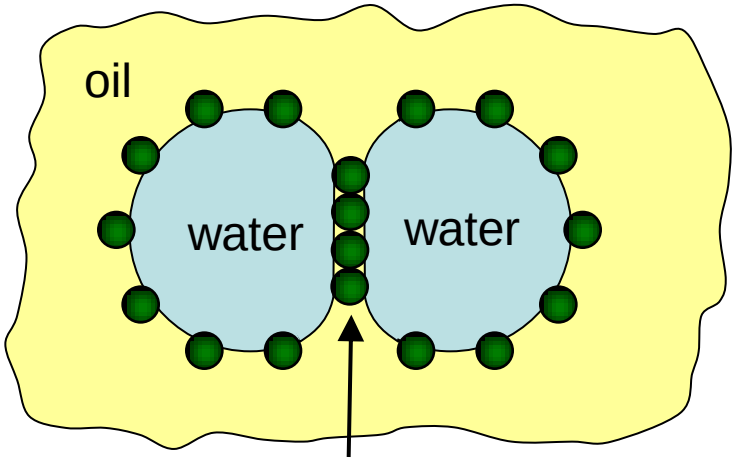
Particle-Stabilised Emulsions

Stabilising Mechanisms

hydrophilic particles $\theta = 65^{o}$

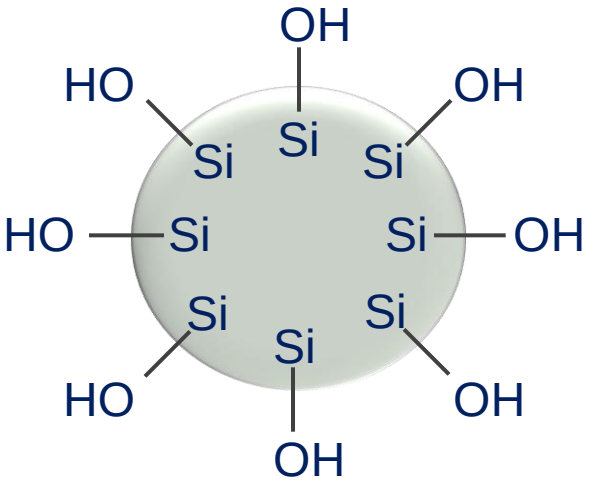


hydrophobic particles $\theta = 152^{o}$

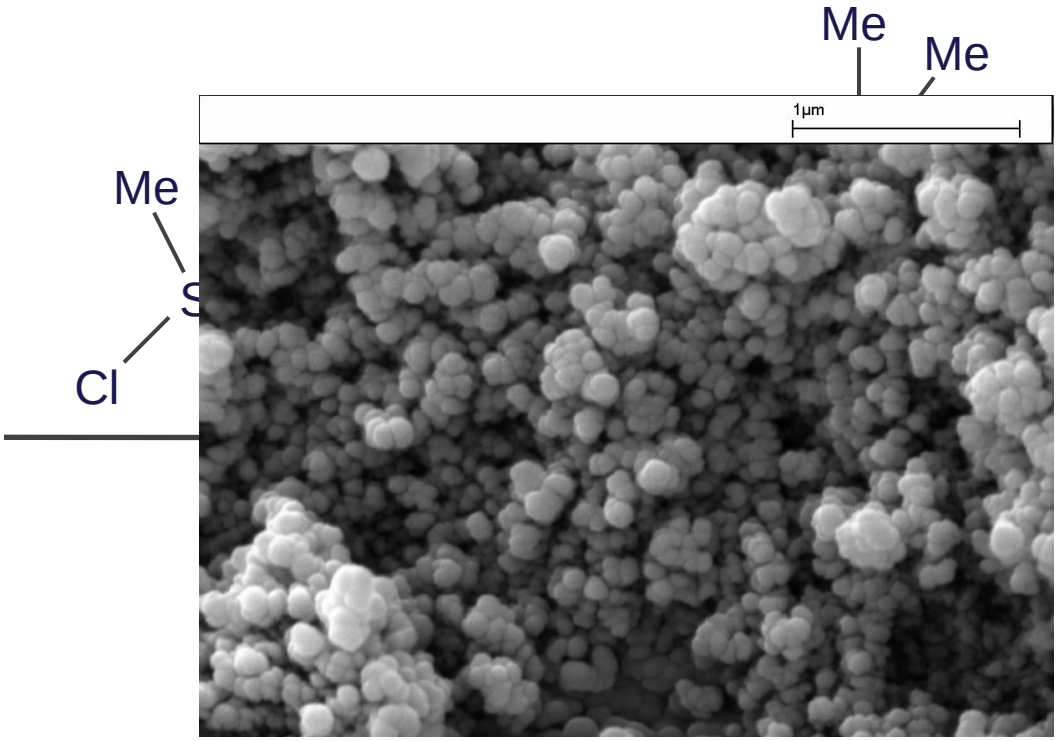


EMULSION INVERSION

- **Fumed silica nanoparticles**
- **20-30 nm primary particle diameter**



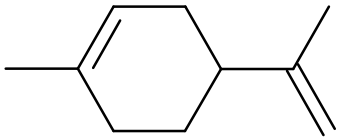
100% SiOH, hydrophilic



< 100% SiOH, more hydrophobic

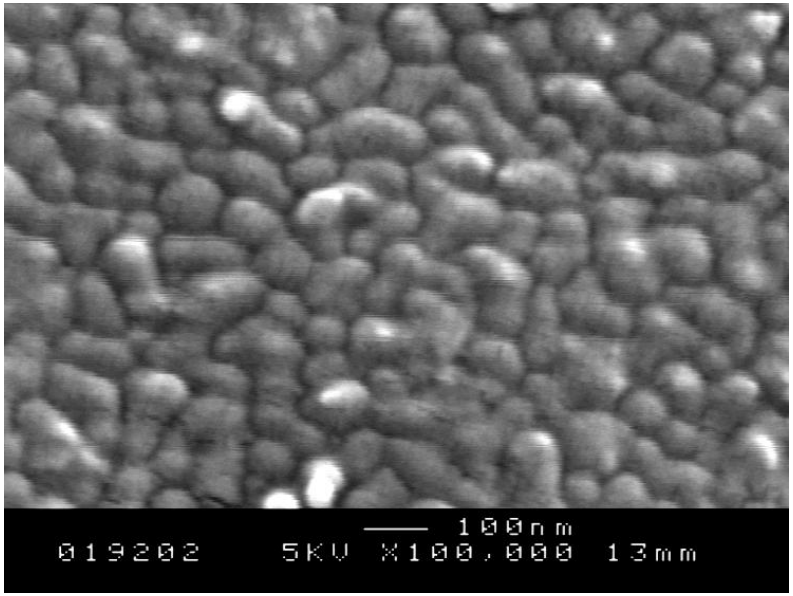
INFLUENCE OF PARTICLE WETTABILITY

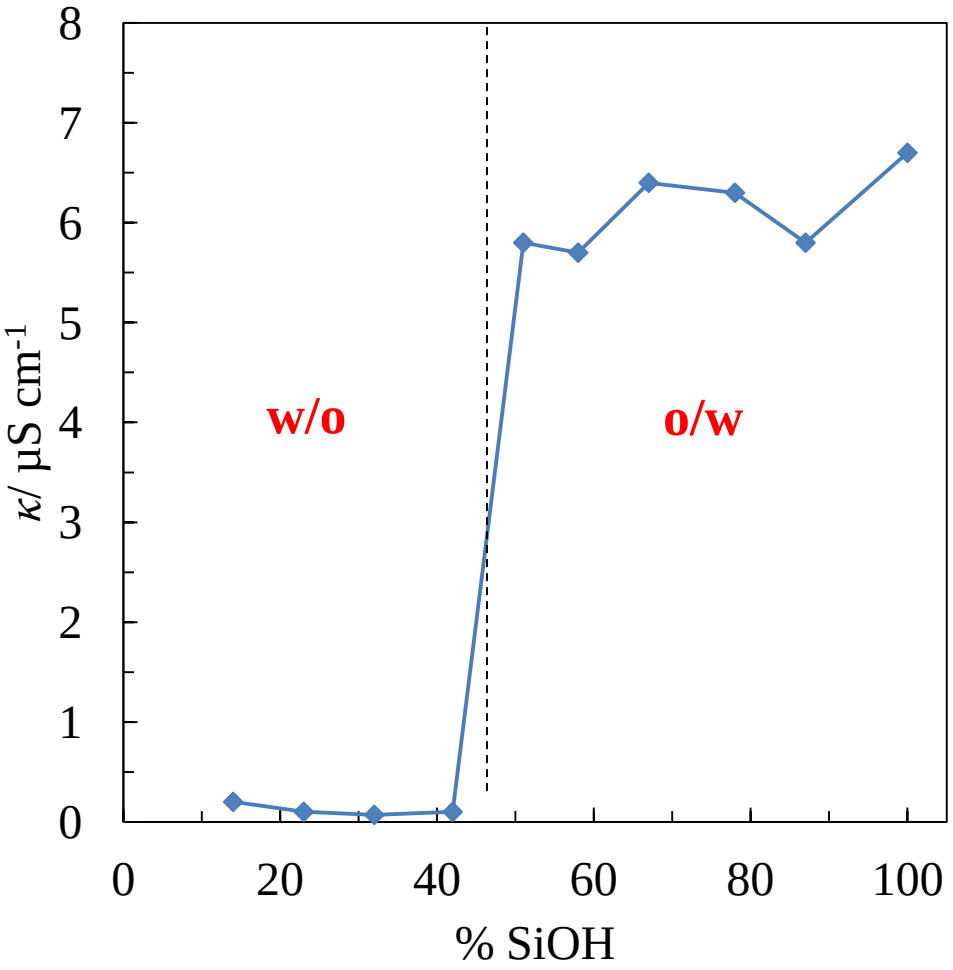
- **Limonene oil**



γ_{ow} = 40.2 mN/m

- **0.1 wt.% particles**
- **ϕ_w = 0.5**

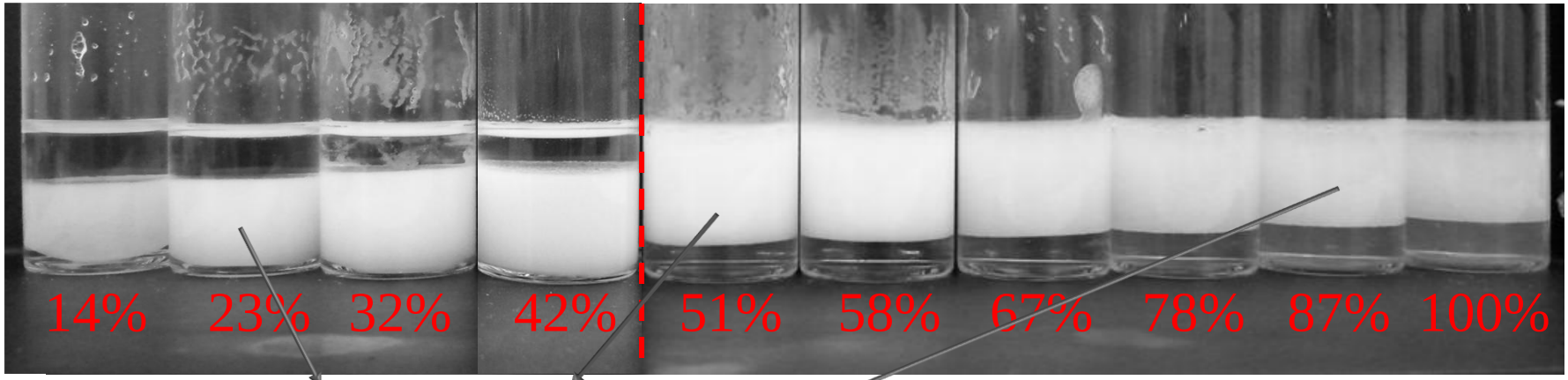


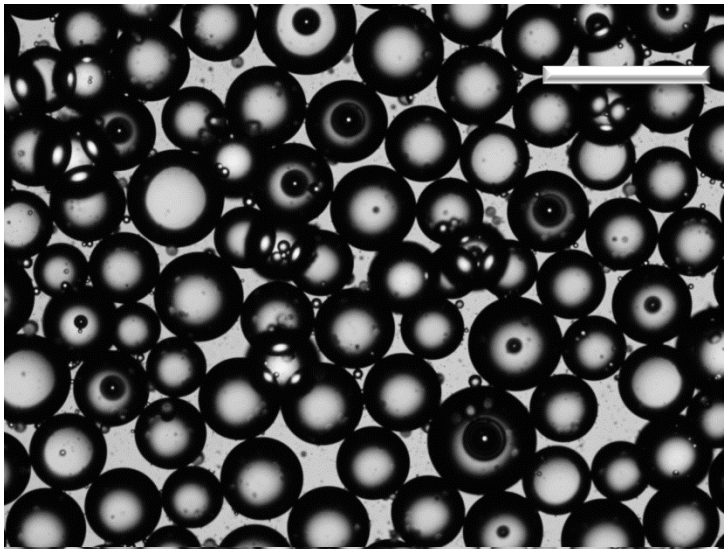


- **Phase inversion occurs at 47% SiOH**

TRANSITIONAL INVERSION OF OIL-WATER SYSTEM

w/o **o/w**



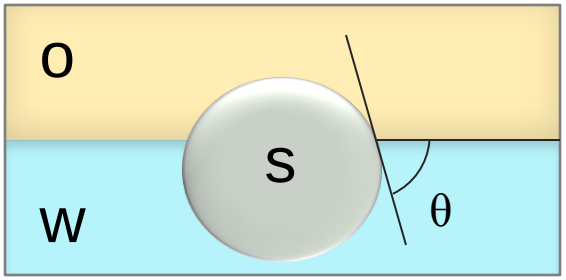


- Stability is greatest at phase inversion
- Drop size is smallest at phase inversion

Scale bar = 500 μm

THEORY: CALCULATING CONTACT ANGLE

$$\cos\theta_{ow} = \frac{\gamma_{so} - \gamma_{sw}}{\gamma_{ow}}$$ *vs.* % SiOH



(a) γ_{ow}: by experiment

limonene 40.2, benzyl acetate 18.4 mN m^{-1}

(b) γ_{sw}: Owens & Wendt, *J. Appl. Polym. Sci.*, **13**, 1741 (1969).

$$\gamma_s = \gamma_s^d + \gamma_s^p$$ dispersion & polar

SOLID-WATER INTERFACIAL ENERGY

$$\gamma_{sw} = \gamma_s + \gamma_w - 2\sqrt{\gamma_s^d \gamma_w^d} - 2\sqrt{\gamma_s^p \gamma_w^p}$$

100% SiOH $\gamma_s^d = 42.0\ mN\ m^{-1};\ \ \gamma_s^p = 34.0\ mN\ m^{-1}$

0% SiOH $\gamma_s^d = 22.0\ mN\ m^{-1};\ \ \gamma_s^p = 0.9\ mN\ m^{-1}$

(c) γ_{so}: SOLID-OIL INTERFACIAL ENERGY

$$\gamma_{so} = \gamma_s + \gamma_o - 2\sqrt{\gamma_s^d \gamma_o^d} - 2\sqrt{\gamma_s^p \gamma_o^p}$$

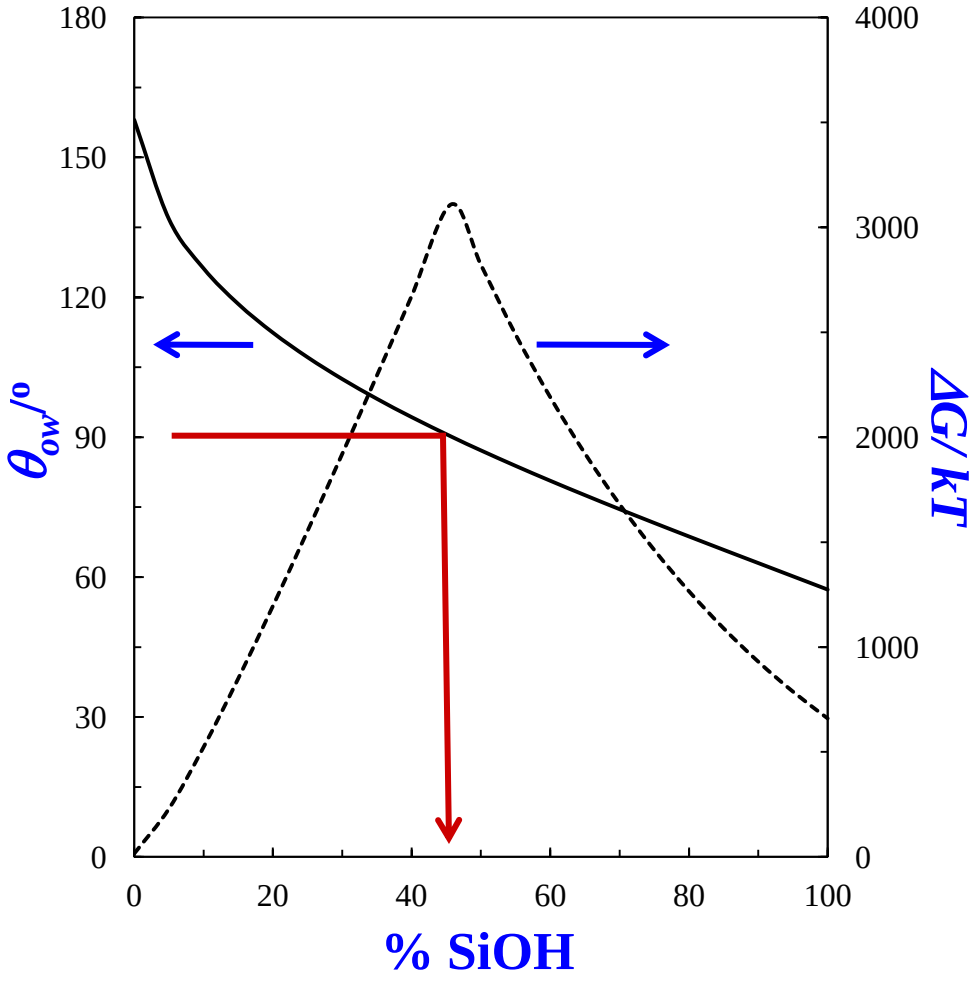
limonene $\gamma_o^d = 28.2\ mN\ m^{-1}$ *and* $\gamma_o^p = 0.6\ mN\ m^{-1}$

benzyl acetate $\gamma_o^d = 29.6\ mN\ m^{-1}$ *and* $\gamma_o^p = 8.3\ mN\ m^{-1}$

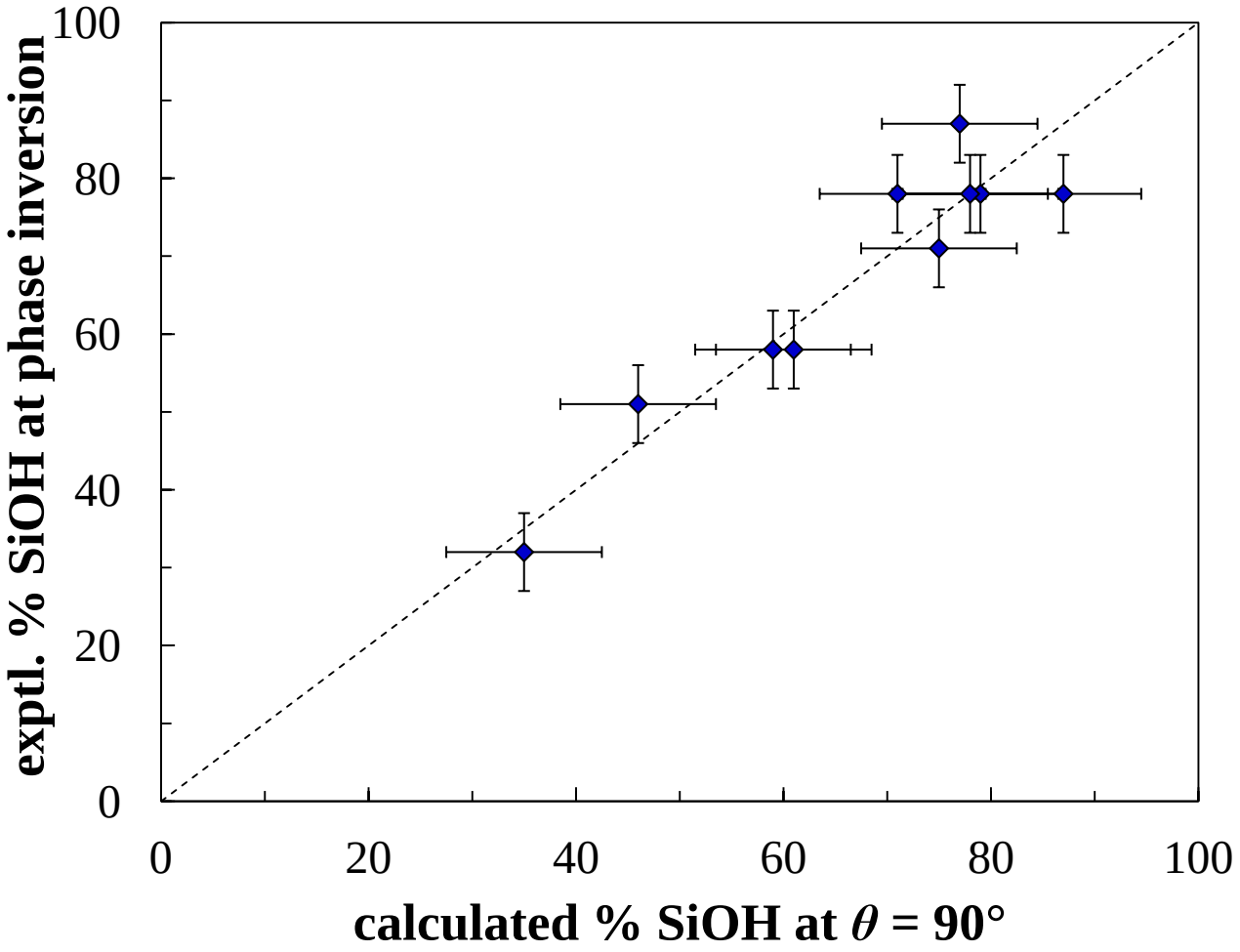
CALCULATED θ_{ow} FOR LIMONENE

Calculated θ_{ow} and ΔG as a function of % SiOH:

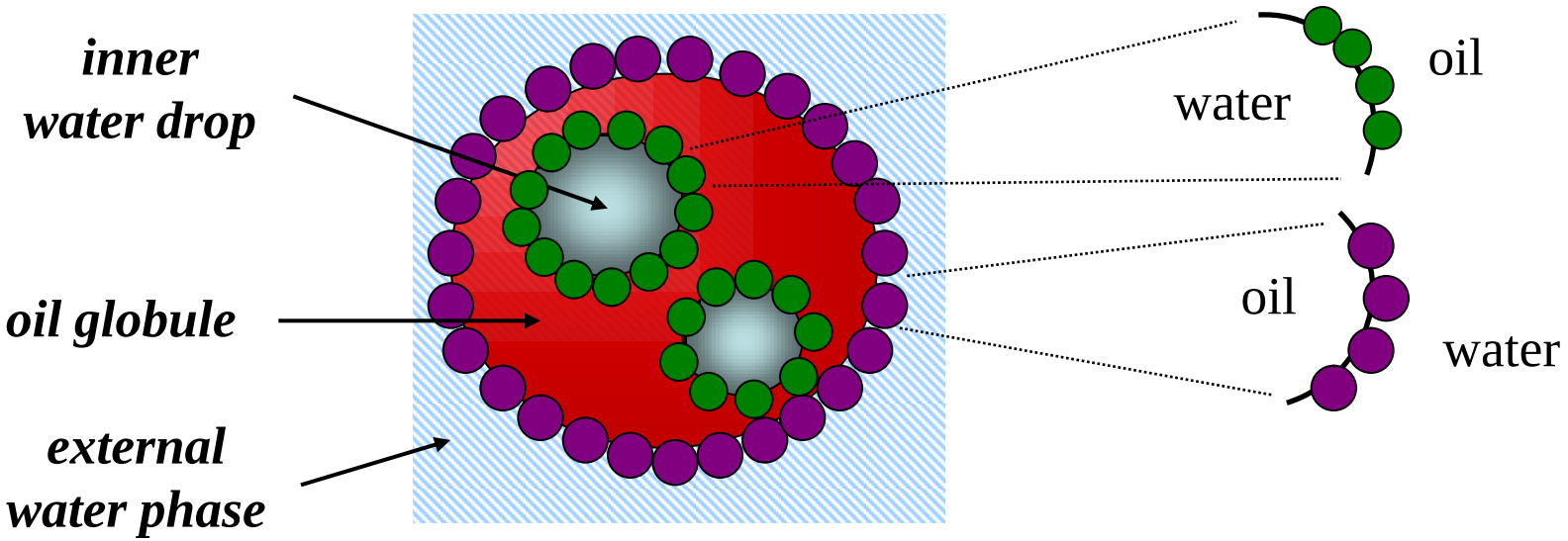
- **Predict phase inversion at 46% SiOH (θ_{ow} = 90°)**
- **Predict stable emulsions for 14 to 100% SiOH**



SUMMARY FOR OILS OF DIFFERENT POLARITY



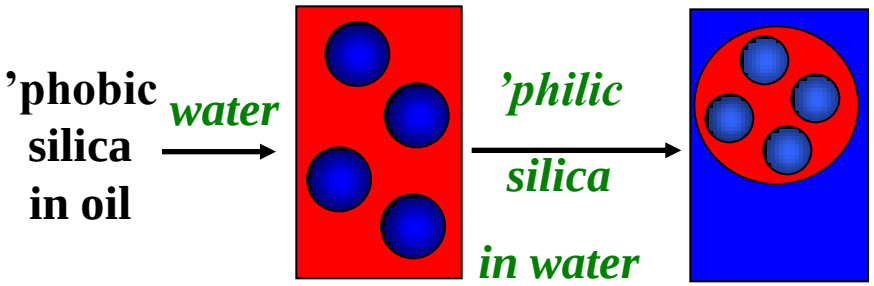
MULTIPLE EMULSIONS



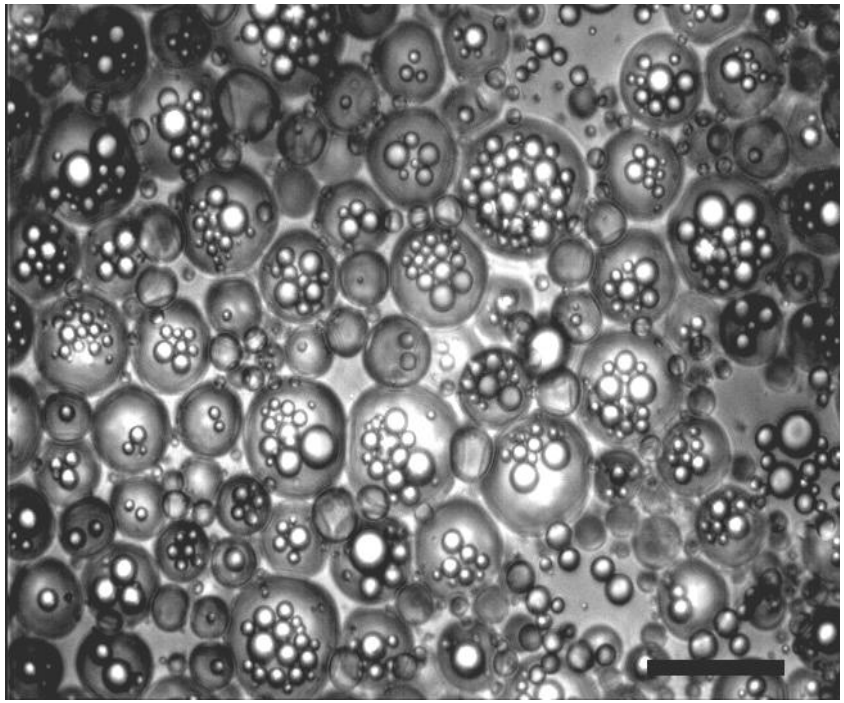
Drugs, enzymes…

Major advantage } **particles stay at interfaces**
no mixing to break the emulsion

W/O/W

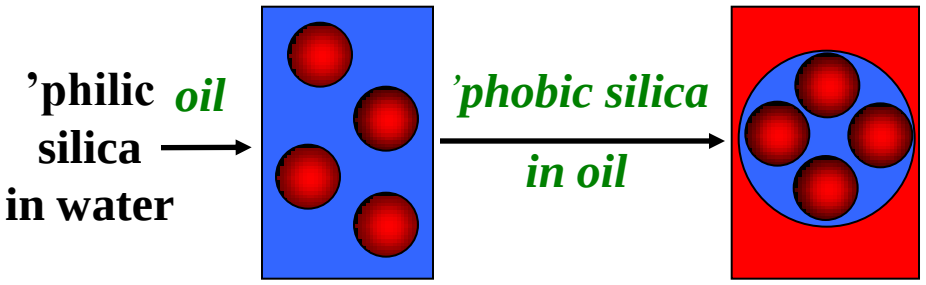


water-in-oil w-in-o-in-w

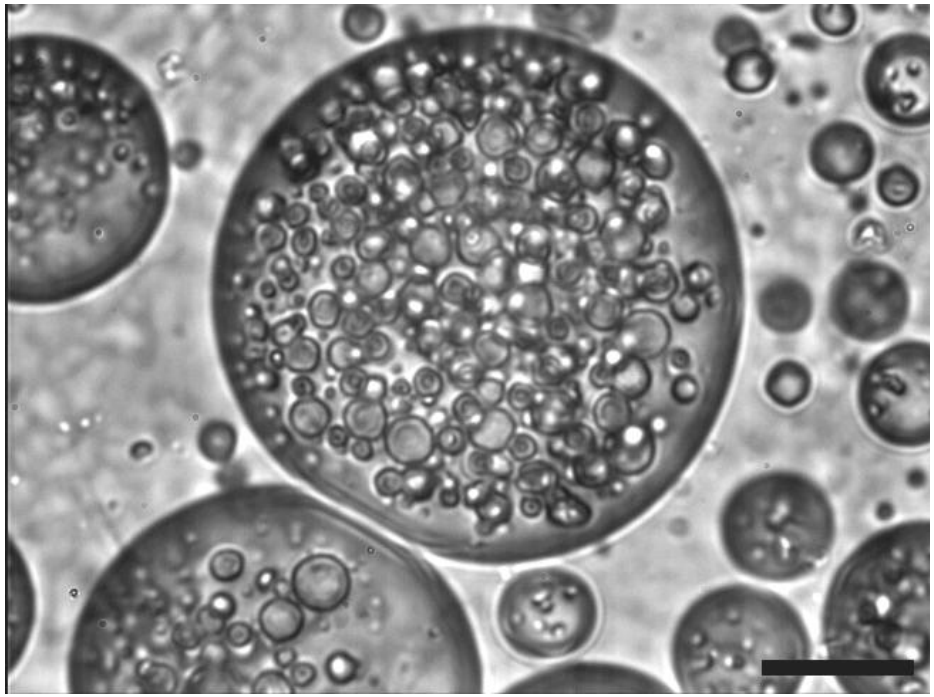


triglyceride 50 μm

O/W/O



oil-in-water o-in-w-in-o



toluene 20 μm

Completely stable for 8 years!

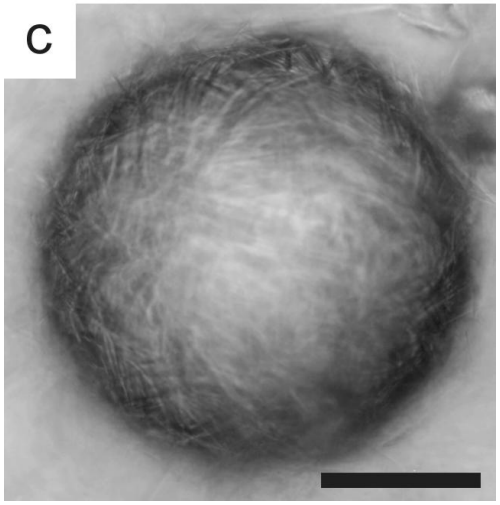
PARTICLE-STABILISED AQUEOUS FOAMS

(a) J.C. Wilson, Ph.D. thesis, 1980

polystyrene latex particles > 2 μm

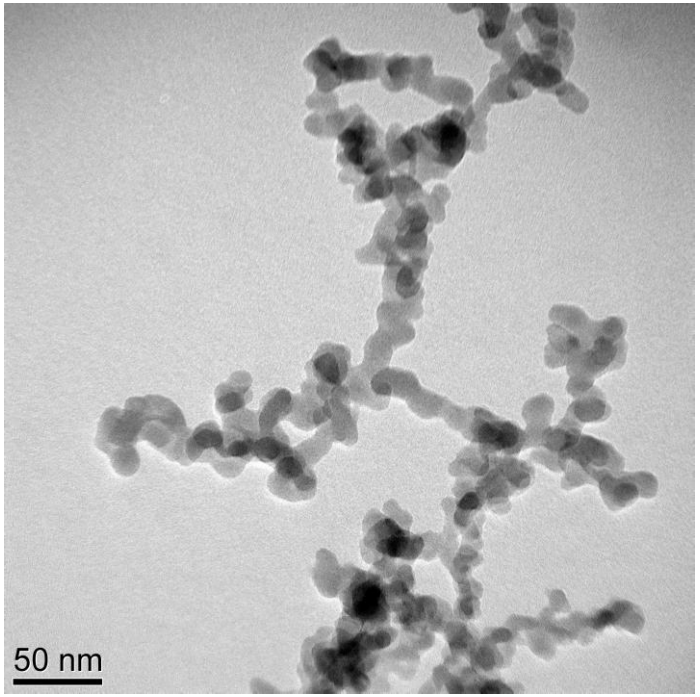
(b) Alargova *et al*., 2004

'hairy' bubbles with 25 x 0.5 μm rods



50 μm

fumed nano-silica
treated with DCDMS
d ~ 30 nm



Effect on foaming of:

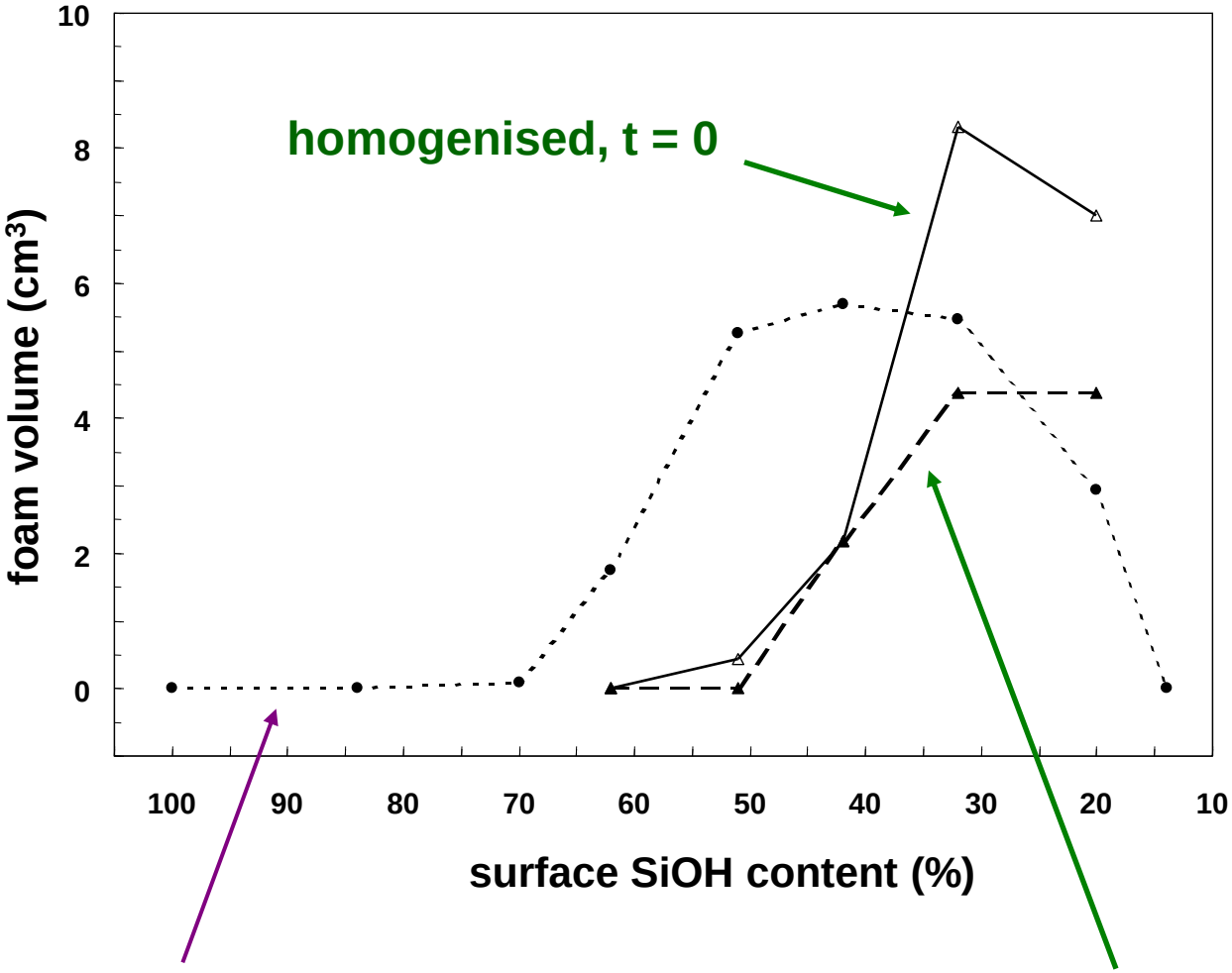
Particle hydrophobicity-vary % SiOH

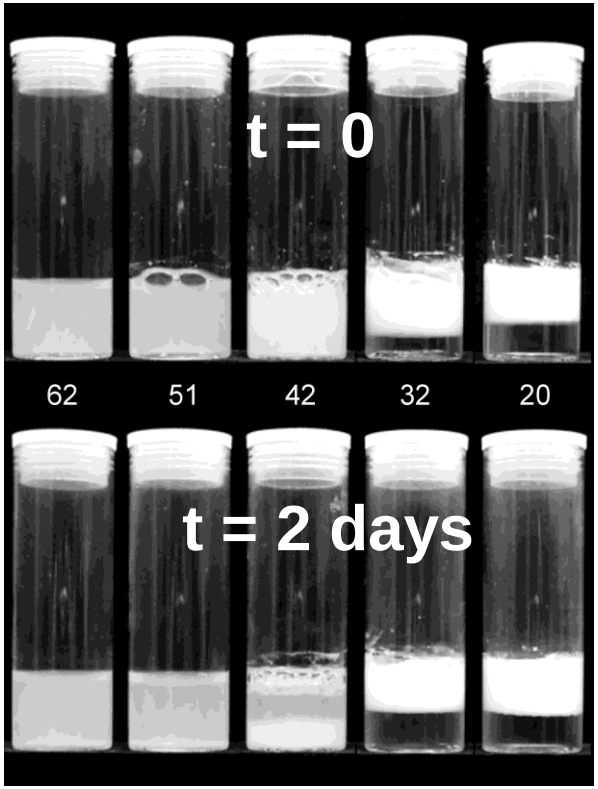
Electrolyte concentration-vary [NaCl]

Silica-stabilised foams: no salt

Powder: on water surface or dispersed in water (using ethanol if necessary)

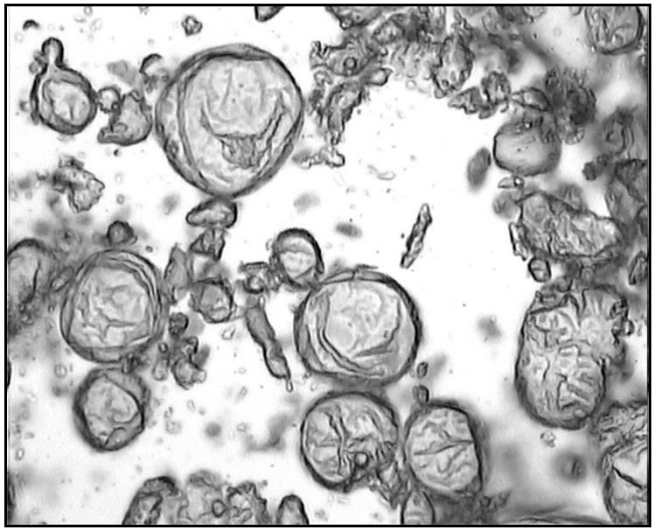
Foams of 1 wt.% made by hand-shaking or using rotor-stator mixer (7 cm^3)



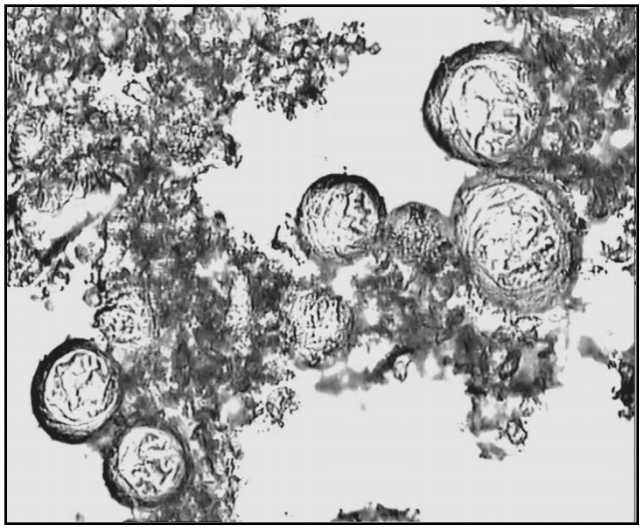


Influence of salt addition on foams

0 M

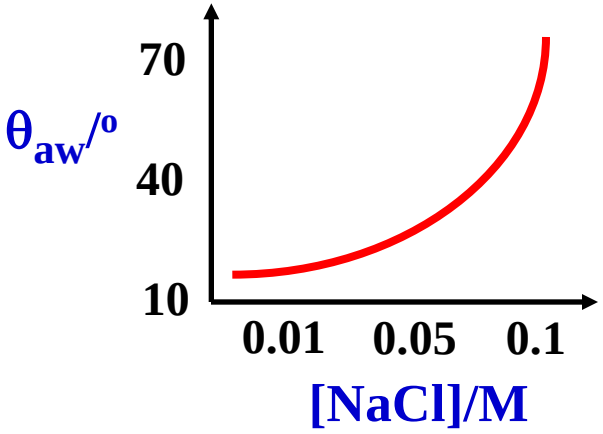


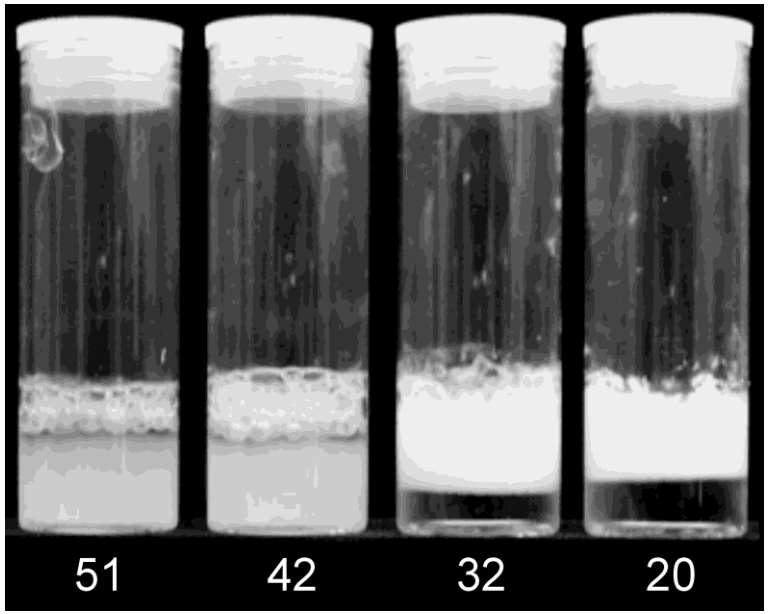
8 mM NaCl



50 μm

Reducing surface charge increases hydrophobicity

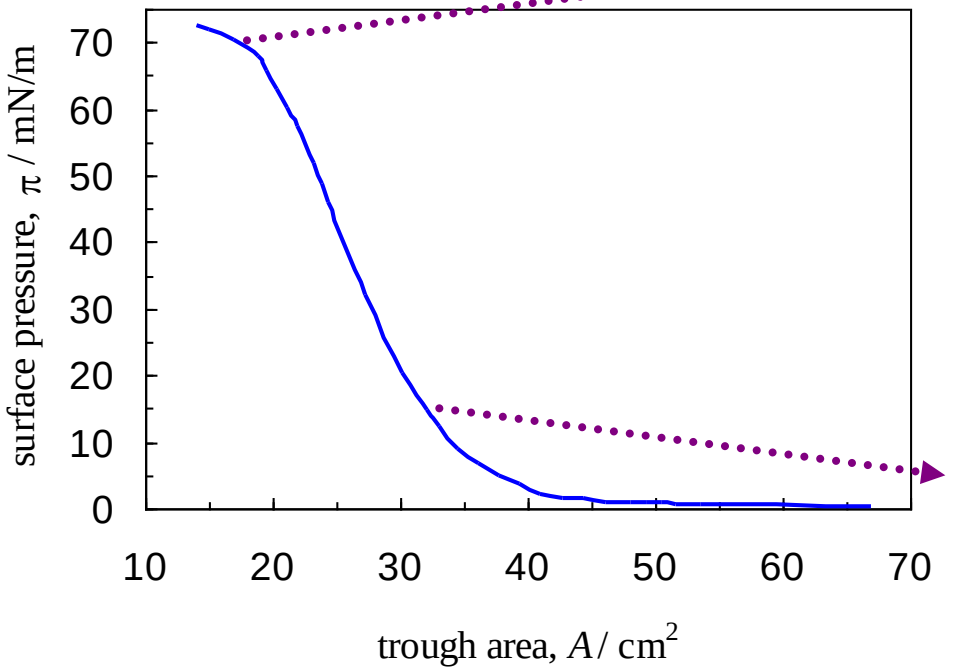


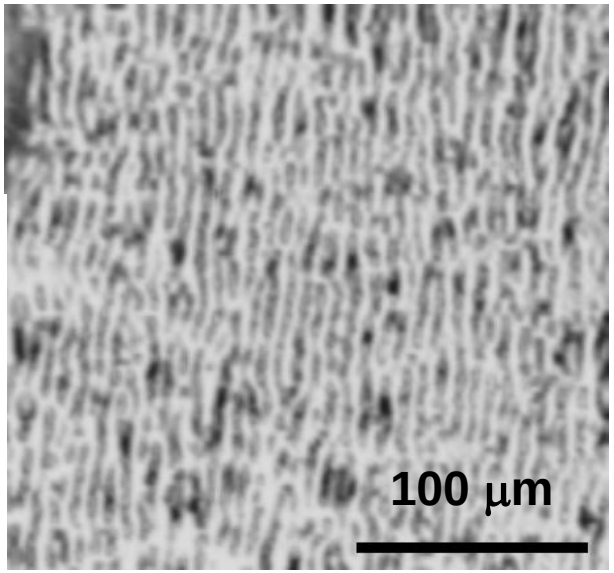


% SiOH

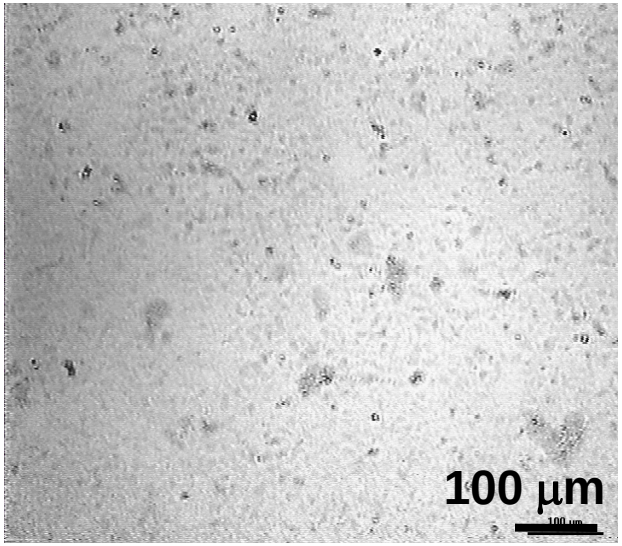
Planar monolayers at air-water surface

Fumed silica, 32 % SiOH spread from chloroform



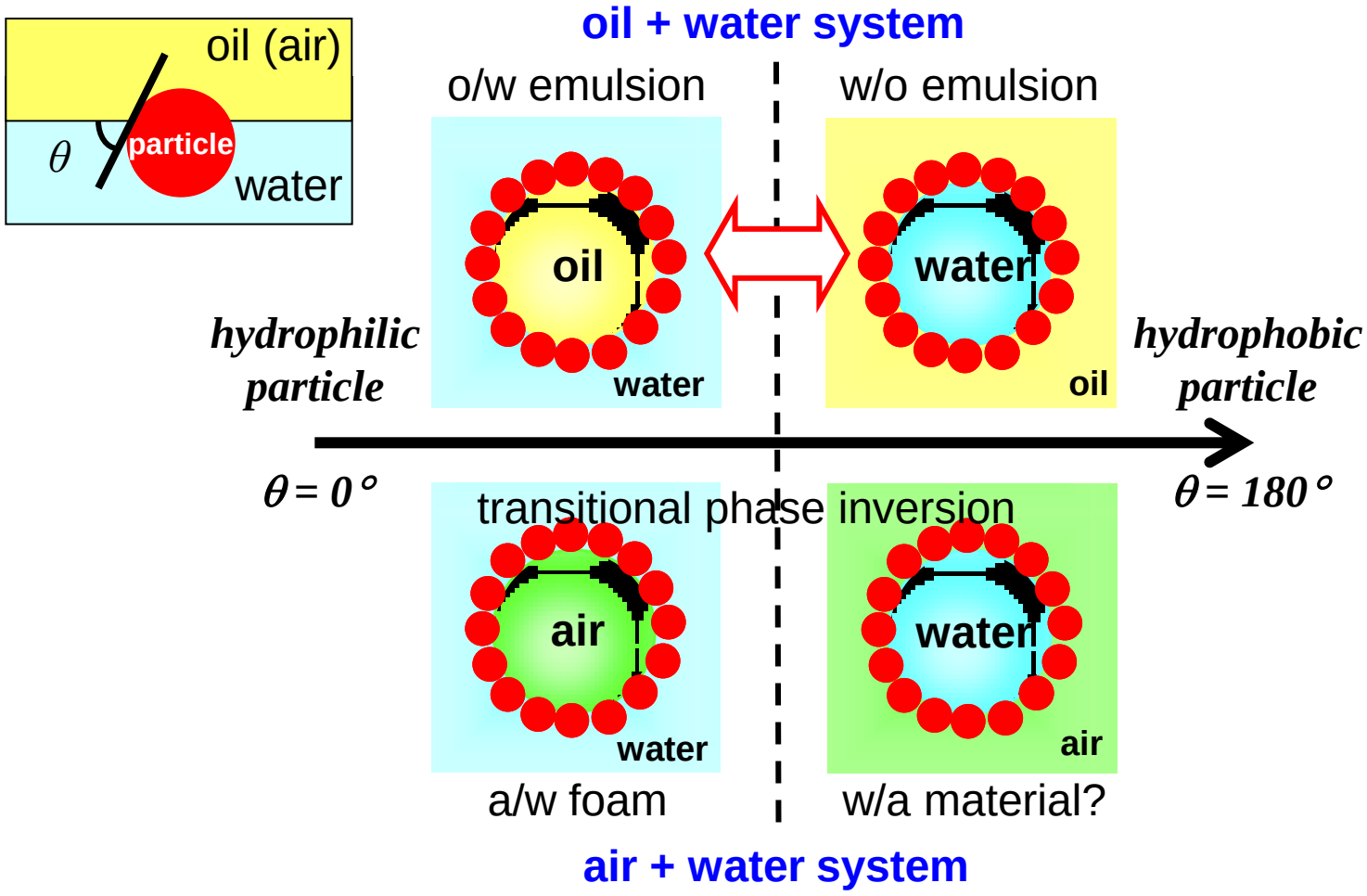


π = 70 mN/m ripples from folding



π = 13 mN/m disordered particle aggregates

EXAMPLES OF PARTICLE-STABILISED DISPERSED SYSTEMS

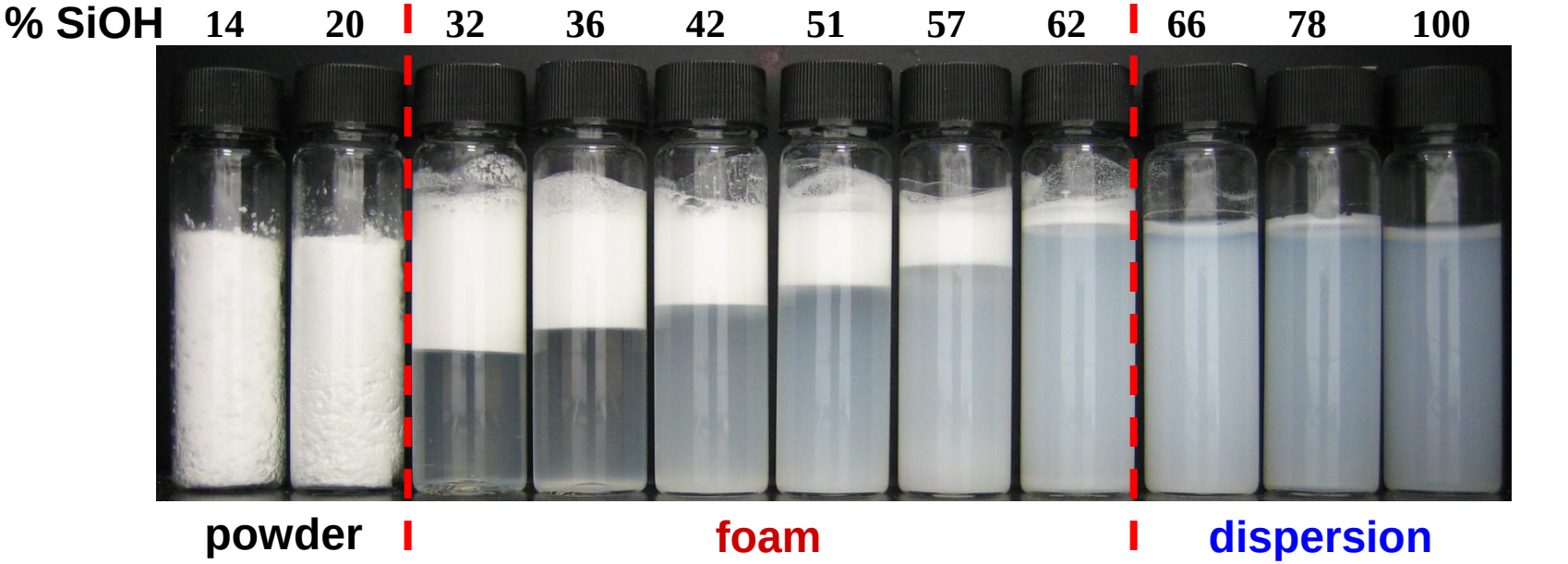


What is the w/a material and how can we phase invert the system?

TRANSITIONAL INVERSION OF AIR-WATER SYSTEM

ϕ_w = 0.056 (95 mL water/1700 mL total vol.)
2 wt.% silica particles (relative to water)
2 weeks after mixing and aeration

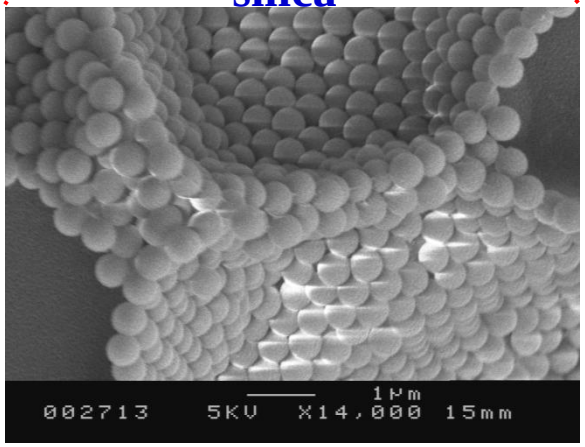
hydrophobic ⟷ *hydrophilic*



Inversion of the curvature of the air-water surface is induced by changing the particle hydrophobicity

Air-in-water foam

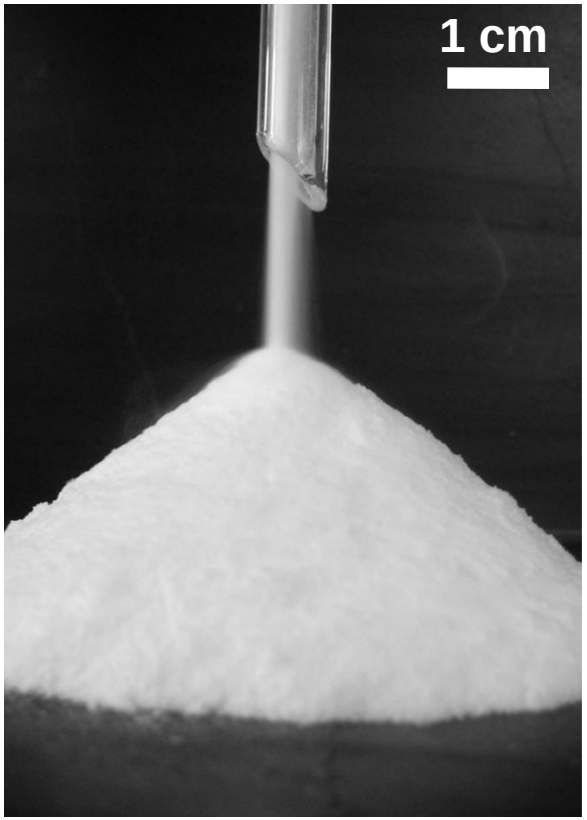
partially hydrophobic silica



phase inversion

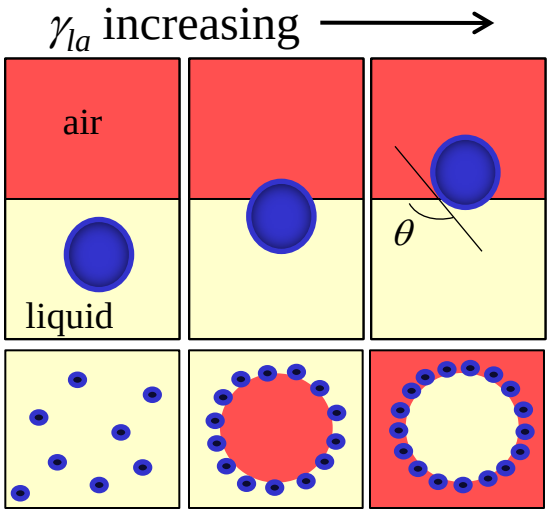
Water-in-air powder

(5 g particles + 95 g water + air)

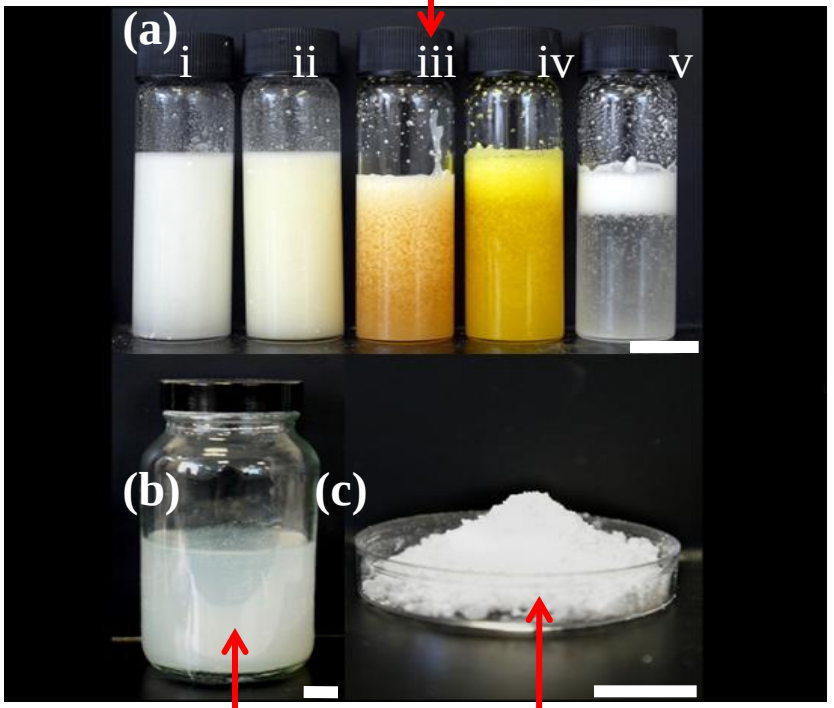


very hydrophobic silica

PARTICLE-STABILISED OIL FOAMS

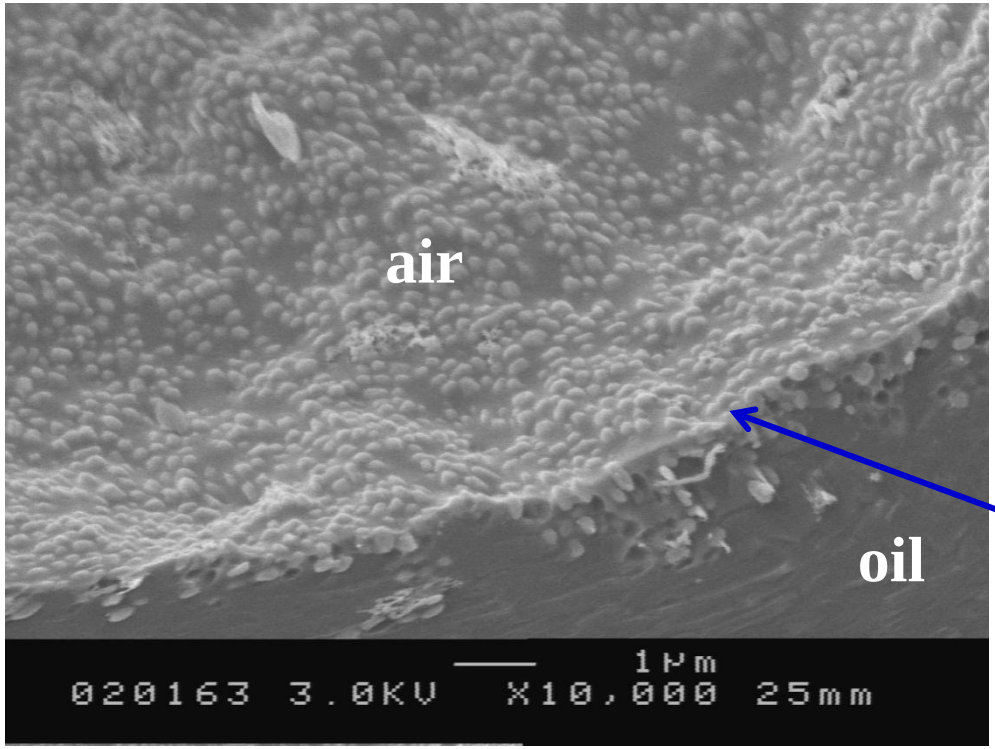


sunflower oil, eugenol, benzyl acetate ..



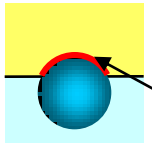
hexane

glycerol



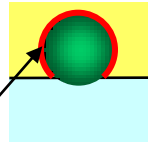
low energy
fluoro- particles

Summary



Hydrophilic particles

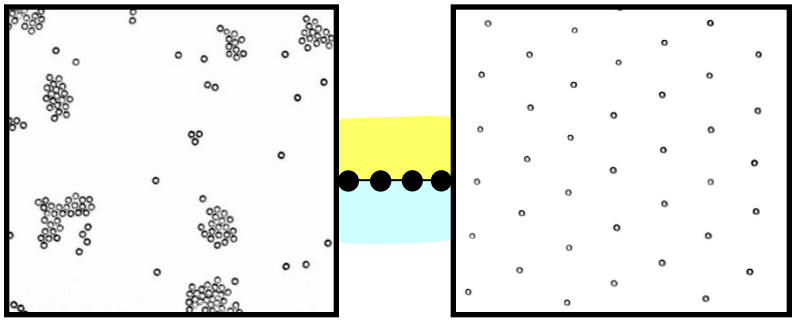
Hydrophobic particles



behave very differently at planar oil-water interface

negligible charge

weak repulsion through the water

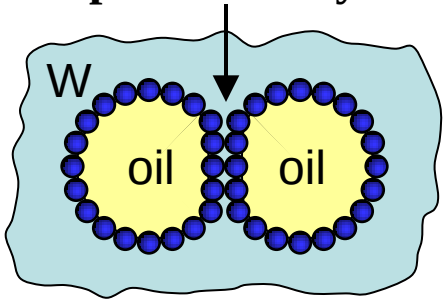


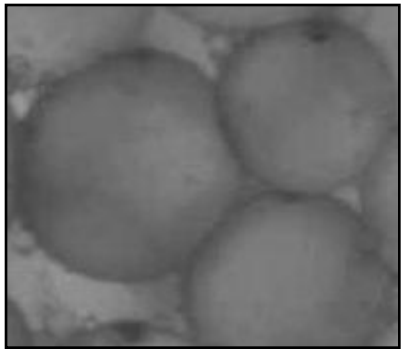
significant charge

strong repulsion through the oil

O/W emulsions

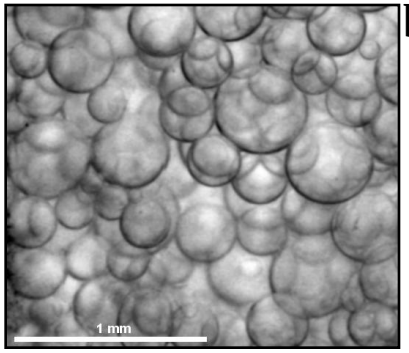
particle bilayer

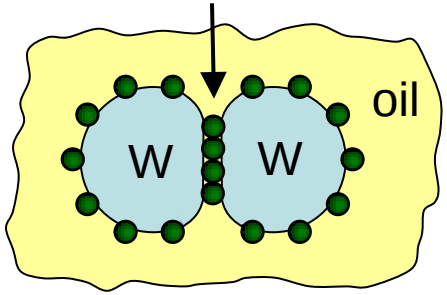




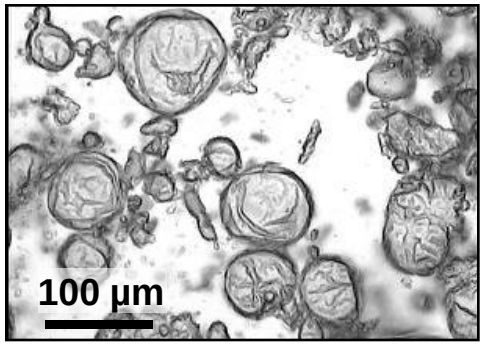
W/O emulsions

bridging particle monolayer





Aqueous & Oil foams with particles



ACKNOWLEDGEMENTS

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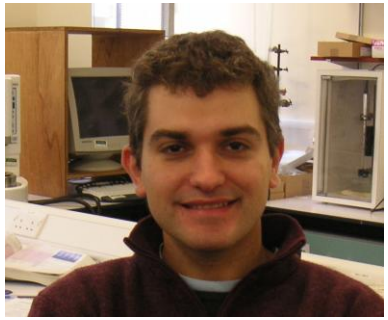

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T.J. Lees

D.A. Braz

Z-G. Cui

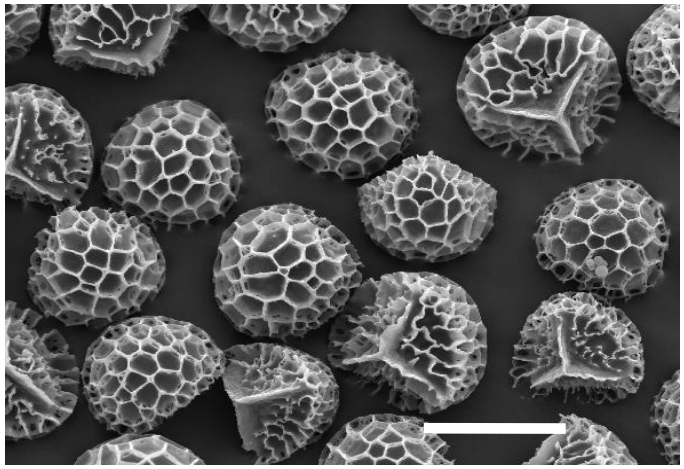
B.L. Holt

NATURALLY OCCURRING PARTICLES

Spores from Club moss - *Lycopodium clavatum*

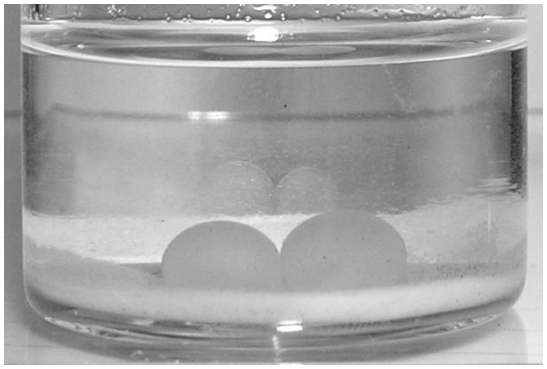
Pyrotechnics, herbal remedies:

diarrhea, dysentery, constipation, eczema!



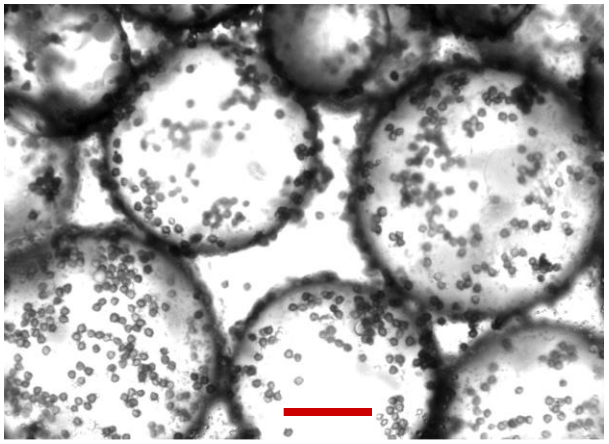
30 μm

2 water drops in oil



1 cm

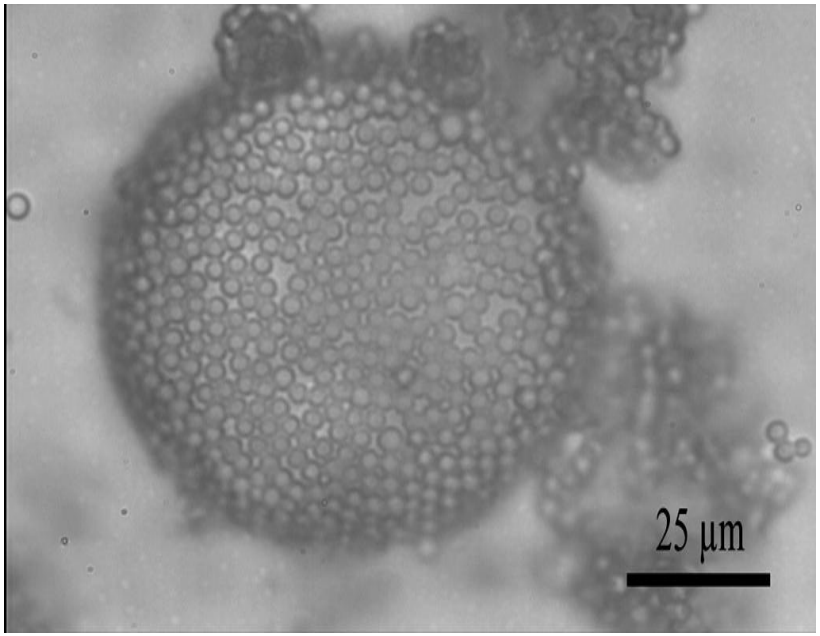
o/w emulsion



200 μm

INTERFACIAL ARRANGEMENT OF PARTICLES

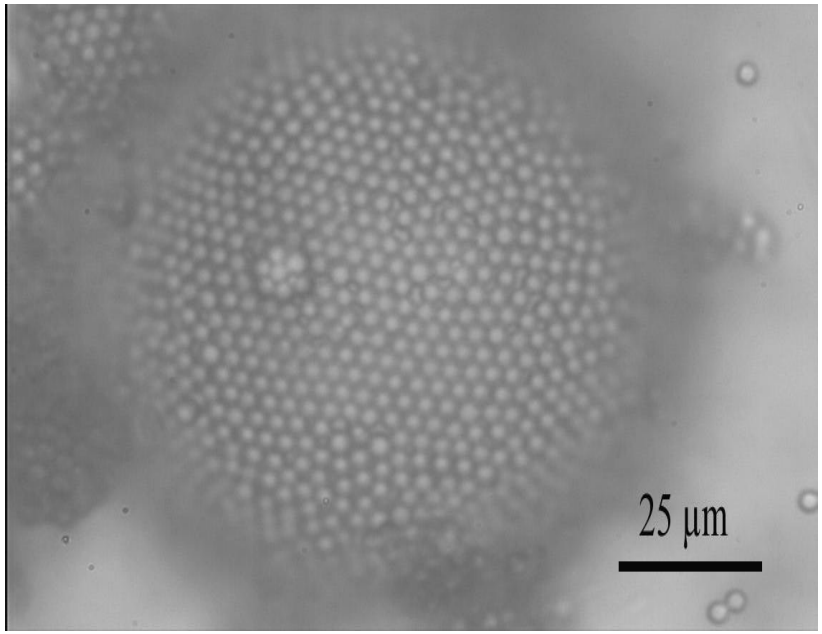
w/o emulsion at pH 6.5



disordered, partially covered monolayer

- particles flocculated in bulk

o/w emulsion at pH 10.1



hexagonally, close packed monolayer

- particles discrete in bulk

Emulsion appearance after 1 year

hexadecane + water (1:1): 1 wt.% of *d* = 200 nm particles

No coalescence!

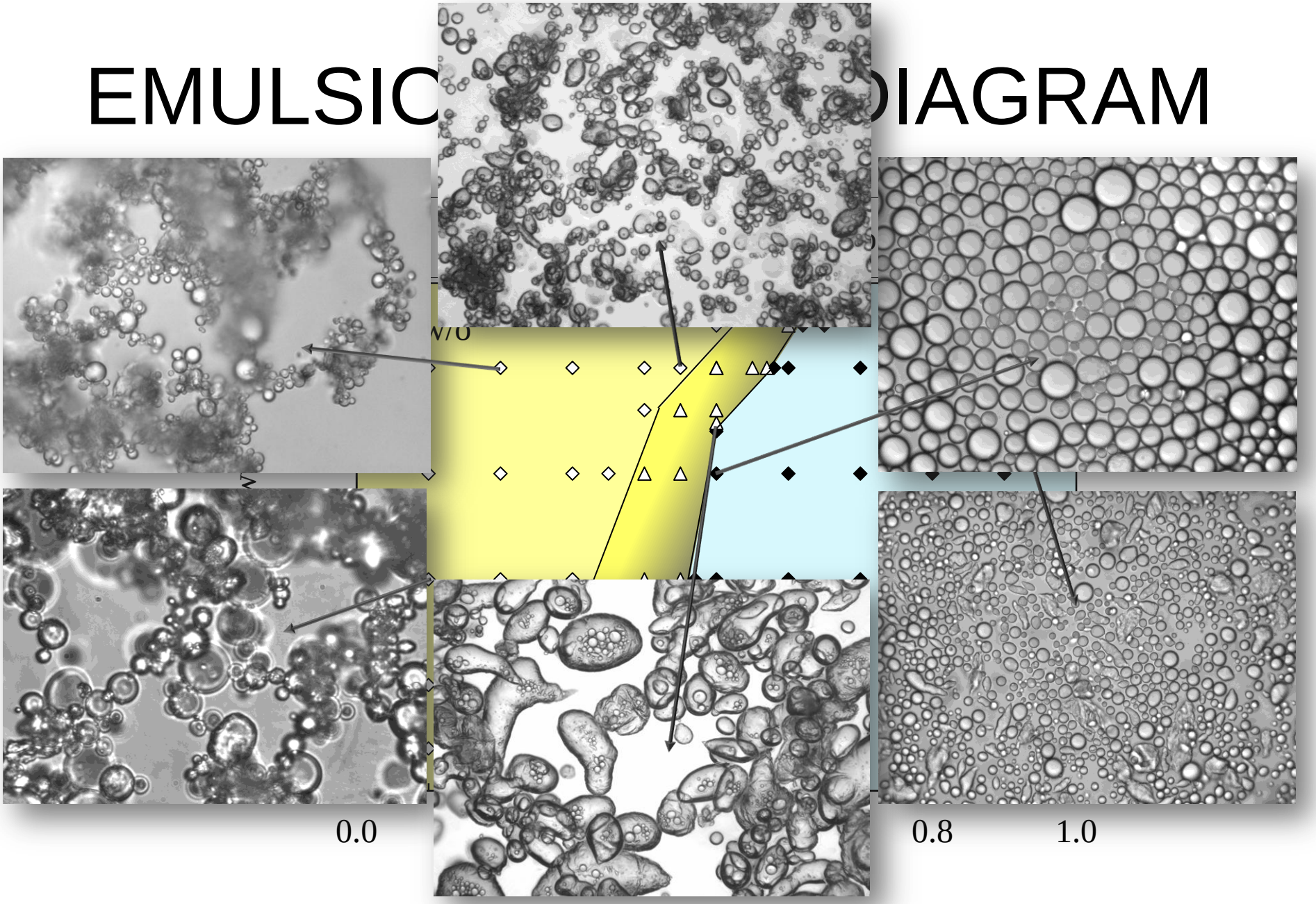
w/o o/w

sedimentation → ← **creaming**

pH: 3.2 6.0 9.2 10.1 10.6 11.0

hydrophobic **partially hydrophobic (pH 5.3)** **hydrophilic**

EMULSIC DIAGRAM



IONISATION OF CARBOXYL GROUPS AT SURFACES

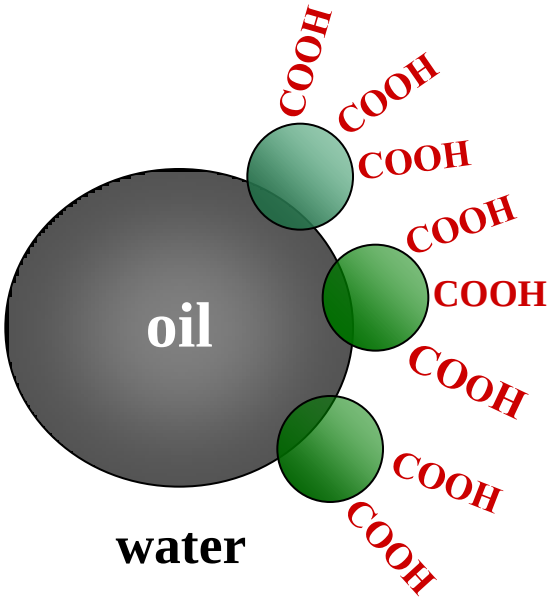
Apparent $pK_{a,s} \approx 10$, *cf.* 5 in bulk

$$\alpha = \frac{[-COO^-]_S}{[-COO^-]_S + [-COOH]_S}$$

$$pH_S = pK_{a,s} - \log[(1-\alpha)/\alpha]$$

$$pH_s = pH_b + [e\psi / 2.303kT]$$

Since $pH_s < pH_b$, ionisation at surfaces weakened *cf.* in bulk



Ionisation hindered two-fold:

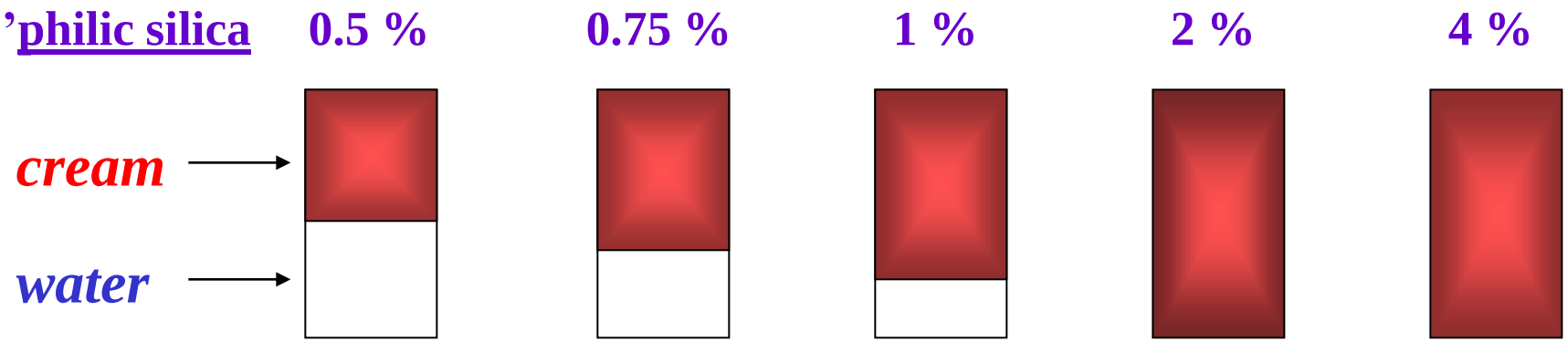
proximity of groups/particle

proximity of particles/drop

EMULSION STABILITY- W/O/W

All w/o/w emulsions stable to coalescence: w drops & o globules

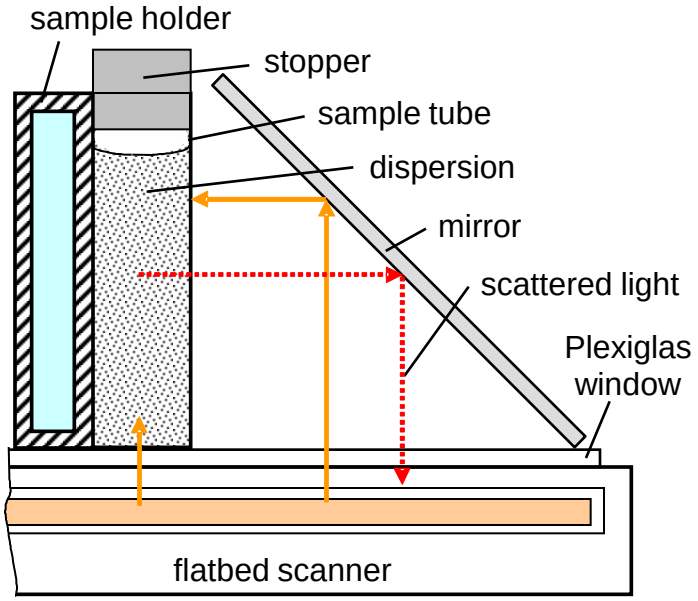
Stability to creaming depends on particle concentration



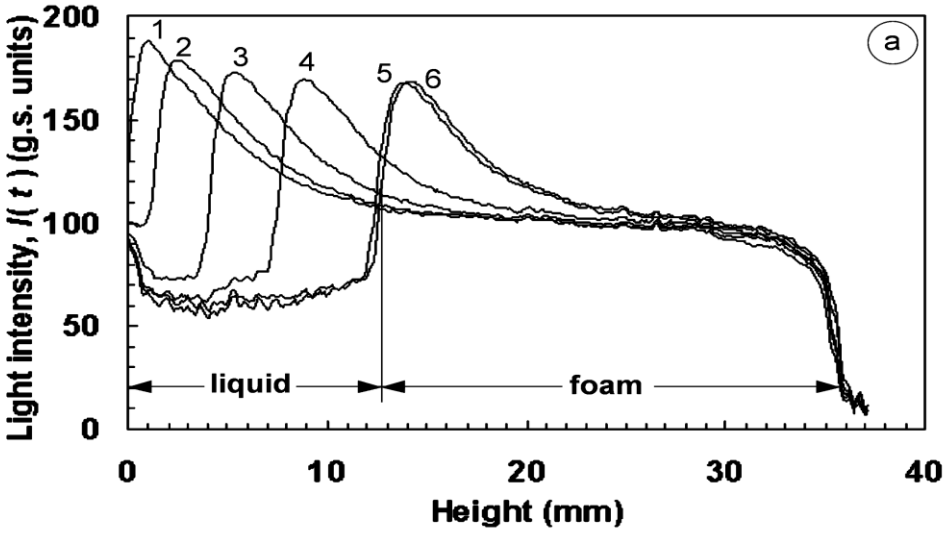
Smaller oil globule size & increased viscosity of continuous water

- creams (ϕ_o=0.7) still stable to coalescence for 4 years

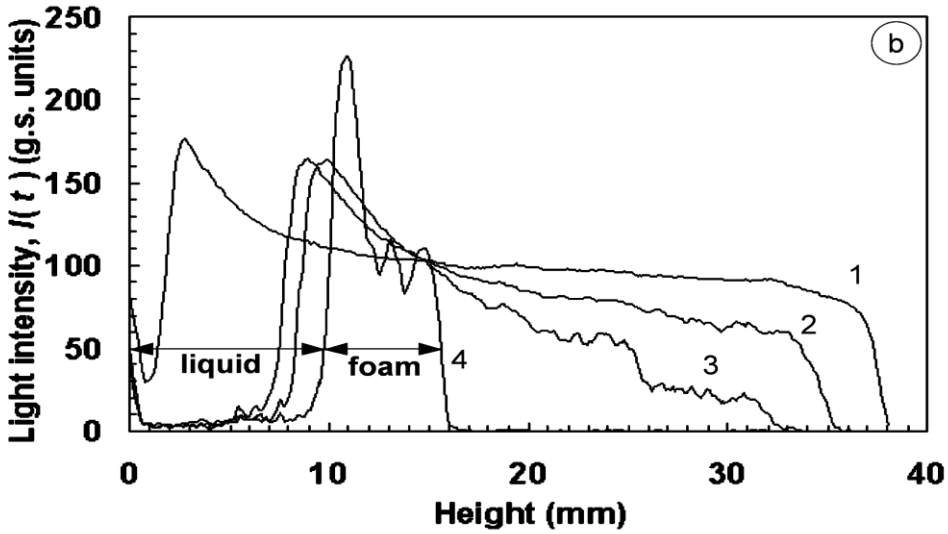
Foam stability by light scattering



silica, 30 s - 72 hr



SDS, 30 s - 6 hr



Particles: drainage of water slow over in few hours

Surfactant: fast water drainage coalescence & ripening

Some Directions for Future Research

charging mechanism ⟺ **particle hydrophobicity ?**

➢ Adsorption kinetics of nanoparticles at fluid interfaces

large R and γ_{ow}
intermediate θ

$$\Delta E_{des} = \pi R^2 \gamma_{ow} (1 \pm \cos\theta)^2$$

small R and γ_{ow}
small or large θ

irreversible particle adsorption **reversible**

$\Delta E_{des} >> kT$ $\Delta E_{des} \leq kT$

➢ Amphiphilic particles

hydrophilic **hydrophobic**

biphilic
(Janus)

➢ Particle-stabilised foams

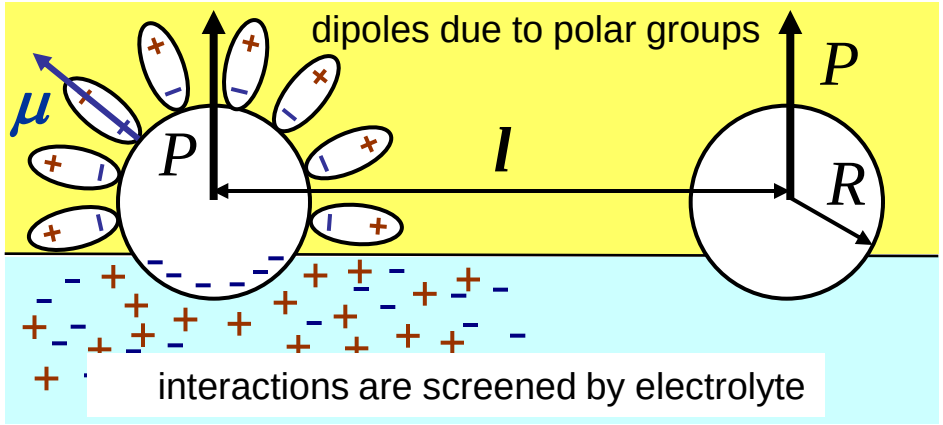
➢ Particles + Surfactants

surfactants decrease γ_{ow}

change θ

competitive adsorption

Particle pair interactions through the oil



Dipolar repulsion (Earnshaw 1993)

$$P = \pi\sigma\mu R^2 \sin^2\theta \quad \text{at} \quad l/2R > 4$$

dipole moment of one polar group

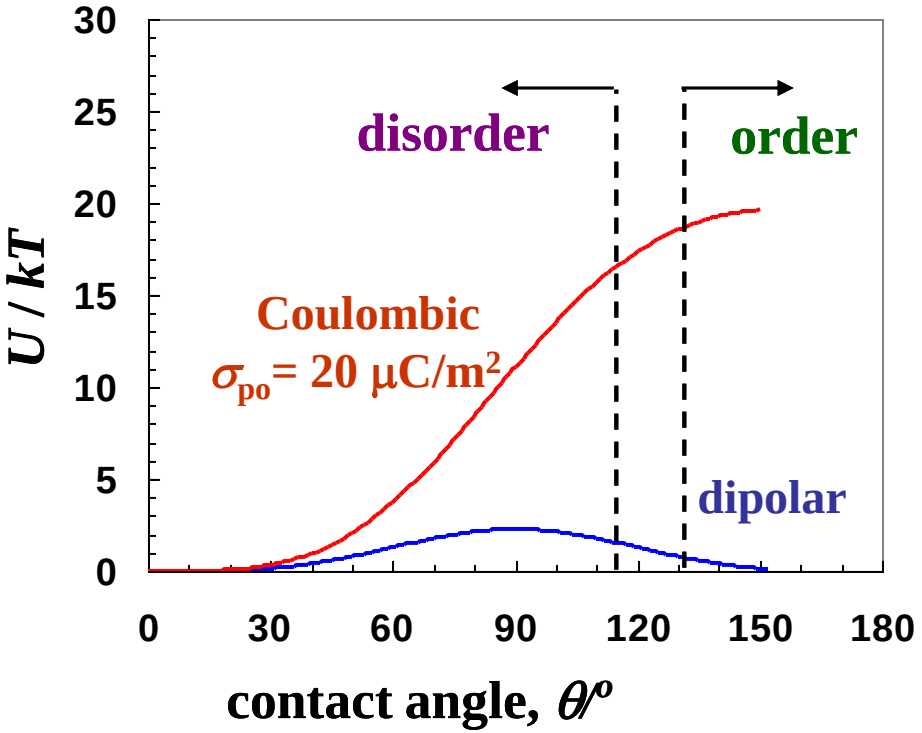
polar groups per unit area

$$U_d = P^2/\left(4\pi\varepsilon\varepsilon_0 l^3\right)$$

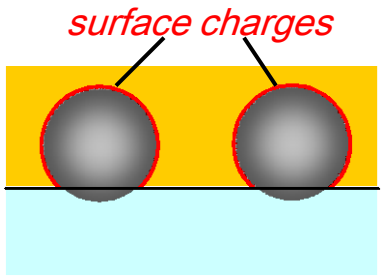
σ = 4.6 OH groups per nm^2

μ = 6.2 10^{-30} C m

octane-water; *R* = 1.5 μm



Coulombic repulsion



$$q_{po} = A_{po}\sigma_{po}$$

σ_{po} ~ 1 - 80 μC m^{-2}

$$U_C = \frac{q_{po}^2}{4\pi\varepsilon\varepsilon_0}\left[\frac{1}{l} - \frac{1}{\sqrt{R^2(3+\cos\theta)^2 + l^2}}\right]$$

Walter Ramsden, M.A., M.D. (1868-1947)

Professor of Biochemistry, Univ. of Liverpool

Fellow of Pembroke College, Univ. of Oxford

Proc. Roy. Soc., **72** (1903), 156

Separation of Solids in the Surface

-layers of Solutions and 'Suspensions'

"*.. bubble retains particles obstinately,*

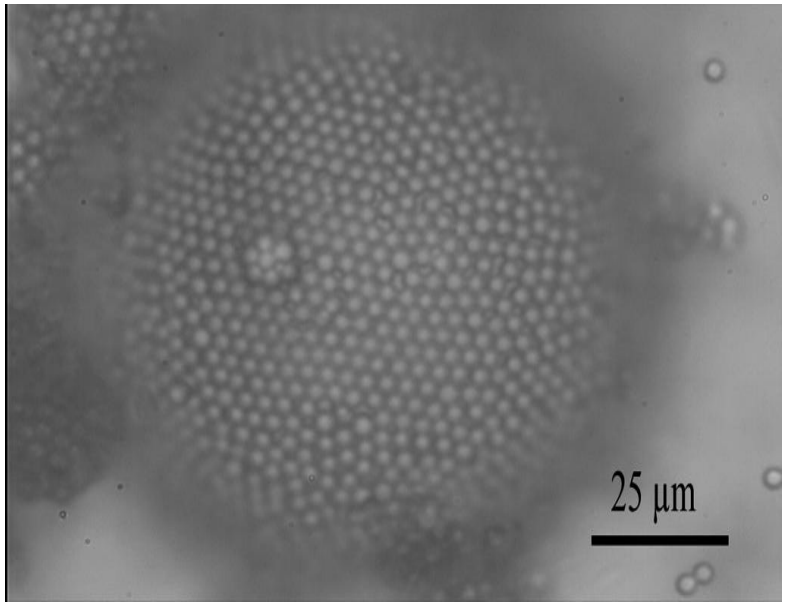
***.. grotesque shapes of globules*."**

John Betjeman, Poet Laureate-to-be; A Few Late Chrysanthemums (1954):

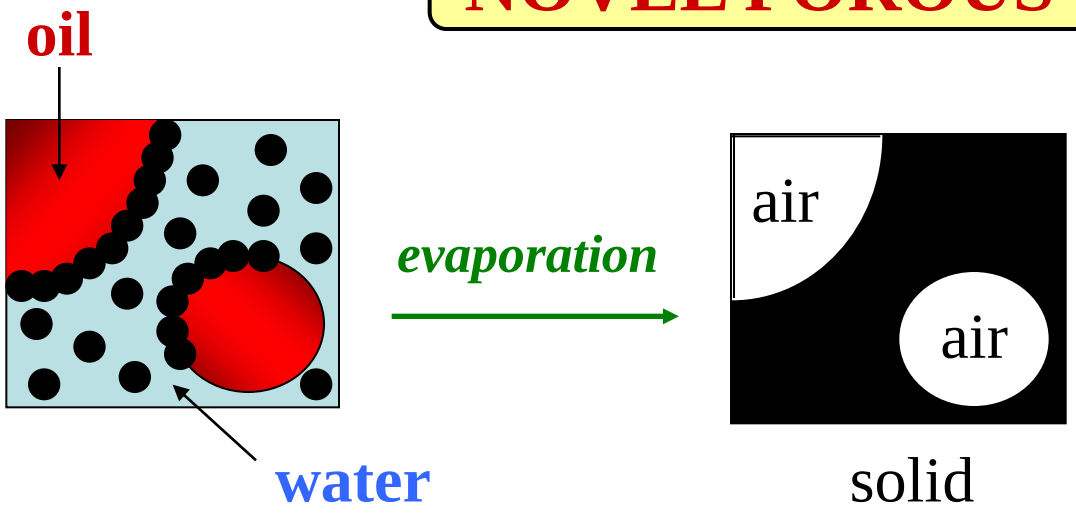
"Dr. Ramsden cannot read The Times obituary to-day, he's dead.

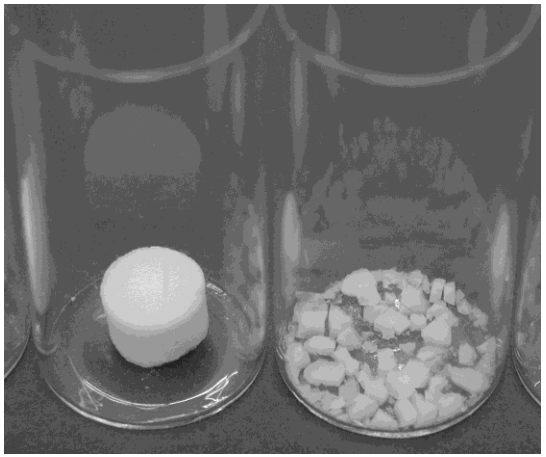
Let monographs on silk worms by other people be thrown away unread, for he who best could understand and criticize them, he lies clay in bed.

Master, Bursar, Senior Tutor, these, his three survivors, all feel old."

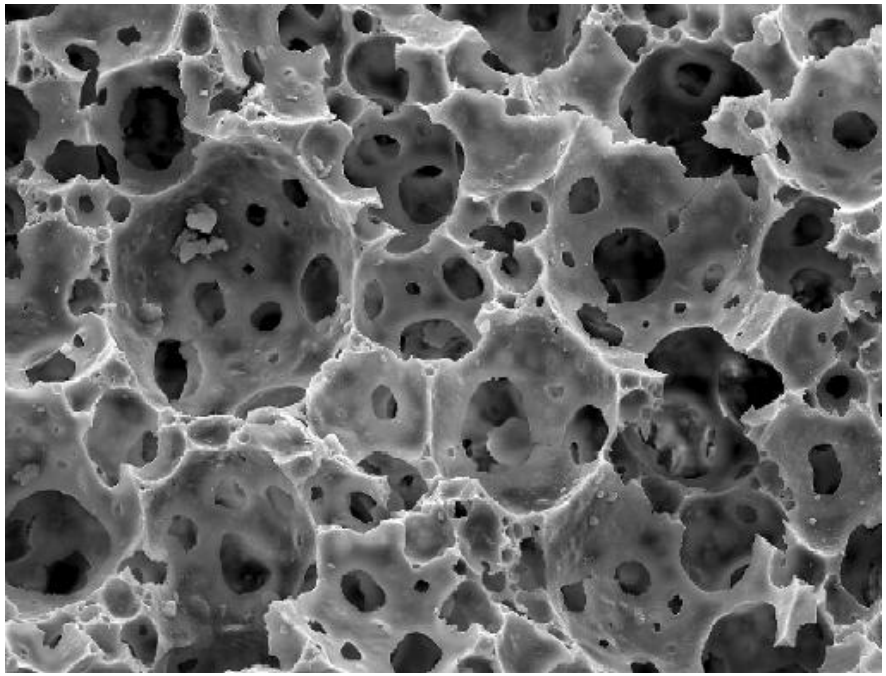

25 µm

NOVEL POROUS SOLIDS





75 % air!



50 μm

emulsion drop size
≈ solid pore size

Uses: sorption media,

filters, catalysts

SHISEIDO
Benefiance
WHITENING

NIVEA
Creme