Interfacial Particles in Emulsions

Eric Dickinson

School of Food Science and Nutrition
University of Leeds

UNIVERSITY OF LEEDS

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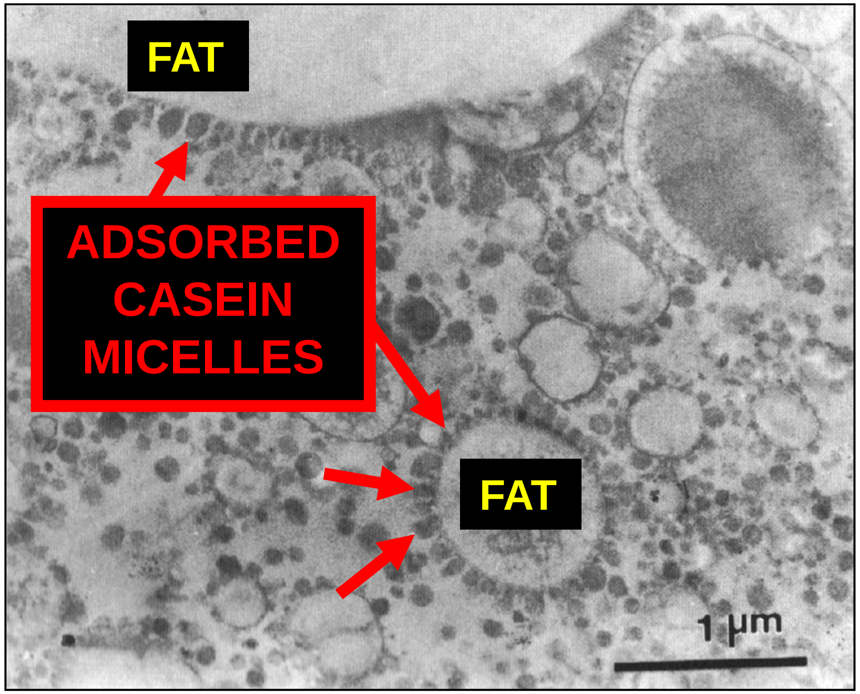
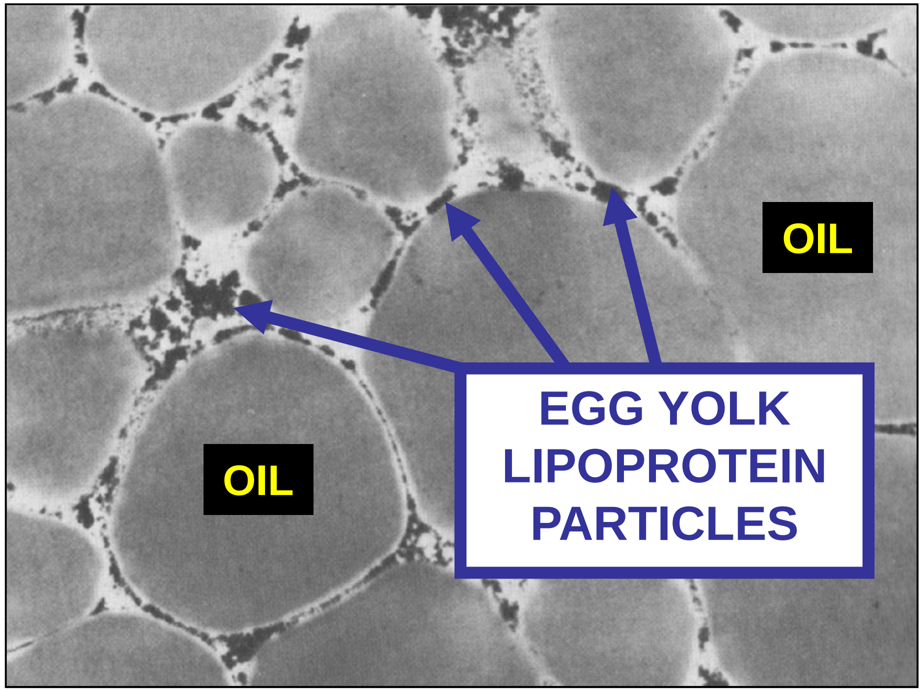
The putative role of dispersed particles in stabilizing food emulsions has long been part of the technical literature

HOMOGENIZED MILK
(3.5 vol% milk fat)



Heertje & Pâques, 1995

MAYONNAISE
(80 vol% vegetable oil)



Holcomb et al., 1990

Many edible emulsions contain solid particles and in certain cases they are recognized as the main stabilizing entities:

fat crystals in butter and margarine

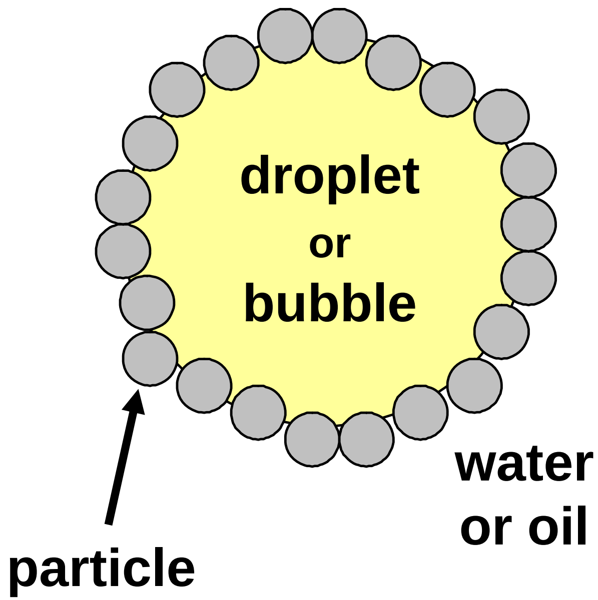
Basic principles of particle stabilization of oil or water droplets apply also to particle stabilization of gas bubbles

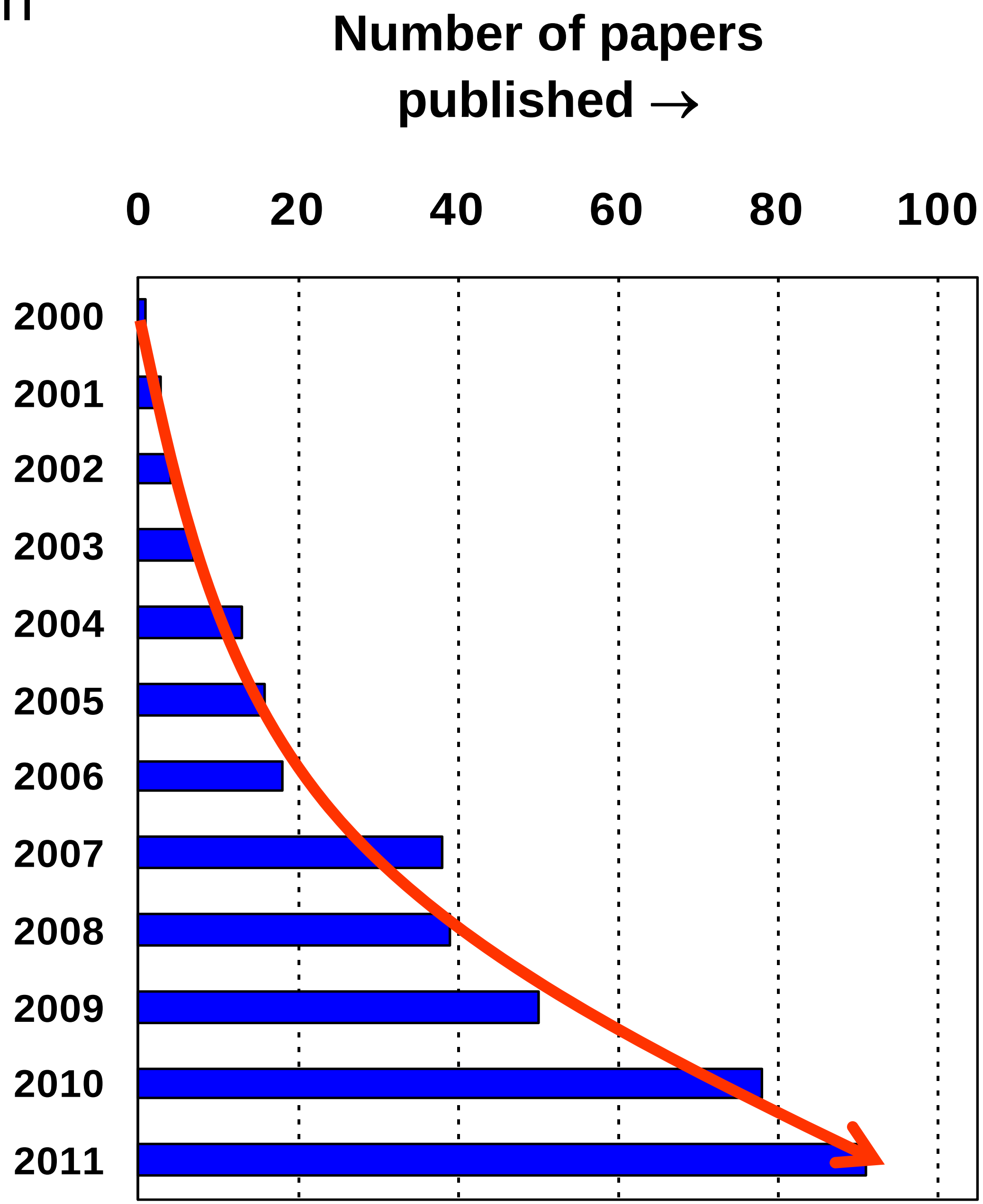
Food foams: bread, cake, meringue, ice-cream, mousse

Many aerated foods contain emulsion droplets

Rapid growth of interest in particle stabilization of emulsions (and foams)

Web of Science search for “Pickering stabilization/stability”





Emulsions stabilized by particles are commonly called

Pickering emulsions

Spencer Pickering showed that basic sulphate of copper, precipitated by the action of lime (CaO) on copper sulphate, was acting as a solid particulate emulsifier for paraffin oil droplets in water

S. U. Pickering, "Emulsions", *Journal of the Chemical Society*, **91**, 2001–2021 (1907).

In fact, the mechanism of stabilizing liquid droplets (and also gas bubbles) by particles had been put forward by **Walter Ramsden** some four years earlier, as acknowledged by Pickering in his 1907 paper

W. Ramsden, "Separation of solids in the surface-layers of solutions and suspensions", *Proceedings of the Royal Society (London)*, **72**, 156–164 (1903).

So they should really be called "**Ramsden emulsions**"

An effective "molecular" emulsifier ...

- rapidly reduces interfacial tension at the freshly formed oil-water interface
- binds strongly to interface once adsorbed
- protects newly formed droplets against flocculation or coalescence

Protection against immediate recoalescence occurs

first *via* dynamic surface tension effects
(Gibbs –Marangoni mechanism)*

later *via* repulsive colloidal interactions
(electrostatic / steric stabilization mechanisms)

* **Emulsifying agent present in the continuous phase (Bancroft's rule)**

Biopolymer emulsifiers → oil-in-water emulsions

PROTEINS

SURFACTANTS ⟺ SOLID PARTICLES

HYDROCOLLOIDS

Qualitative similarity of behaviour...

LOW emulsifier concentration → initally droplets only partly covered

↓

droplets coalesce until their surfaces become covered by dense layer of molecules / particles

HIGH emulsifier concentration → average droplet size depends on oil–water interfacial tension

Surfactants (fast adsorbing) — **<u>equilibrium</u> (static) tension**

Hydrocolloids/proteins (slow adsorbing) — **<u>dynamic</u> tension**

Particle emulsifiers — **tension at <u>bare</u> oil–water interface**

Emulsification involves...

DISRUPTION OF DROPLETS

To disrupt a droplet of radius a requires a pressure gradient

$$\frac{\Delta p}{a} = \frac{2\gamma}{a^2}$$

where Δp is the Laplace pressure and γ the interfacial tension

This implies a pressure gradient ~ 10^{10} Pa m^{-1} (**1 kbar cm^{-1}**)

Due to the high effective interfacial tension and the slow adsorption of dispersed particles, it is **more difficult to make fine emulsions with particle emulsifying agents**

Qualitative similarity of behaviour...

Once an emulsion is formed, stability depends on...

Strength of repulsive interactions between closely approaching droplet surfaces

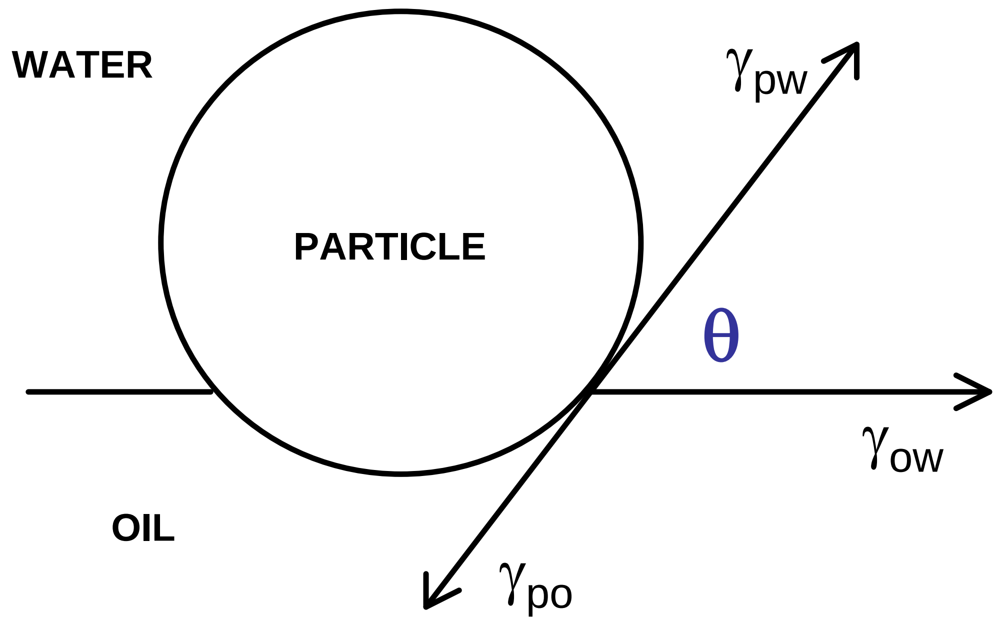
At very low ionic strength (with charged surfaces):

Long-range electrostatic repulsion is important

For moderate or high ionic strength:

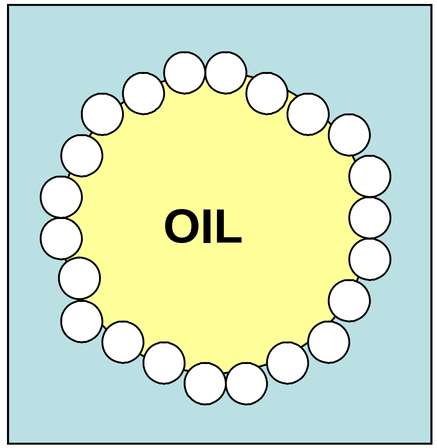
Minimum interdroplet separation is determined by **physical space** occupied by species in adsorbed layer

Location of predominantly hydrophilic spherical particle at oil–water interface



Young's equation:

$$\cos\theta = (\gamma_{po} - \gamma_{pw}) / \gamma_{ow}$$



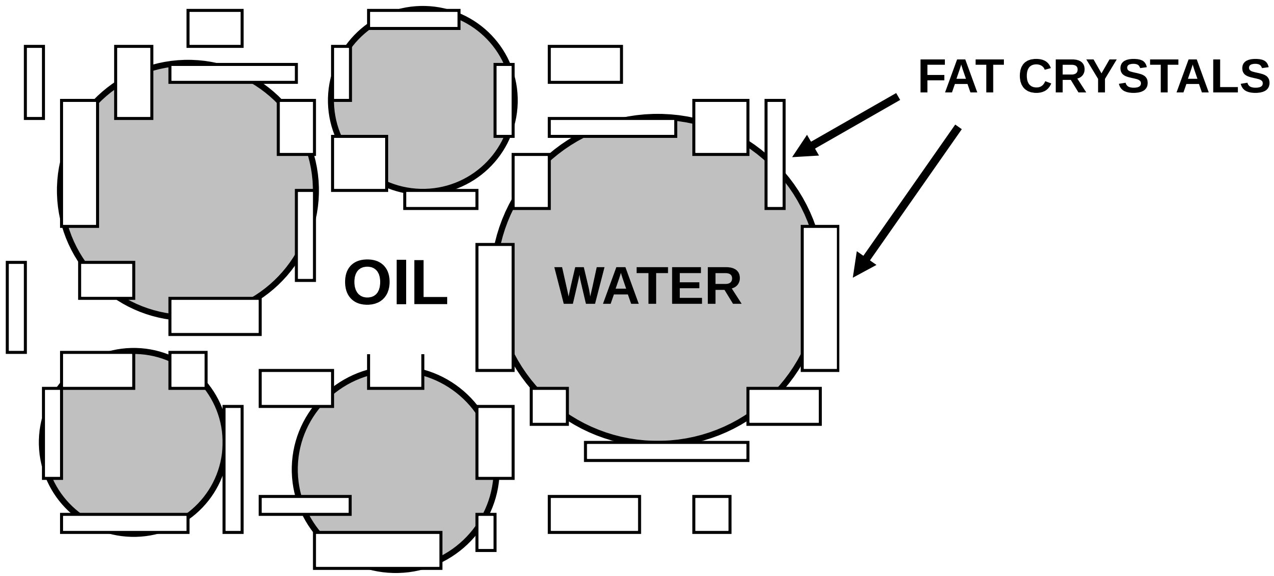
Interfacial tensions:

- γ_{po} **particle–oil**
- γ_{pw} **particle–water**
- γ_{ow} **oil–water**

Contact angle $\theta < 90°$ favours stabilization of oil-in-water emulsion

FINKLE'S RULE

Margarines and water-in-oil fatty spreads are stabilized by fat crystals of high contact angle ($\theta >> 90^\circ$)



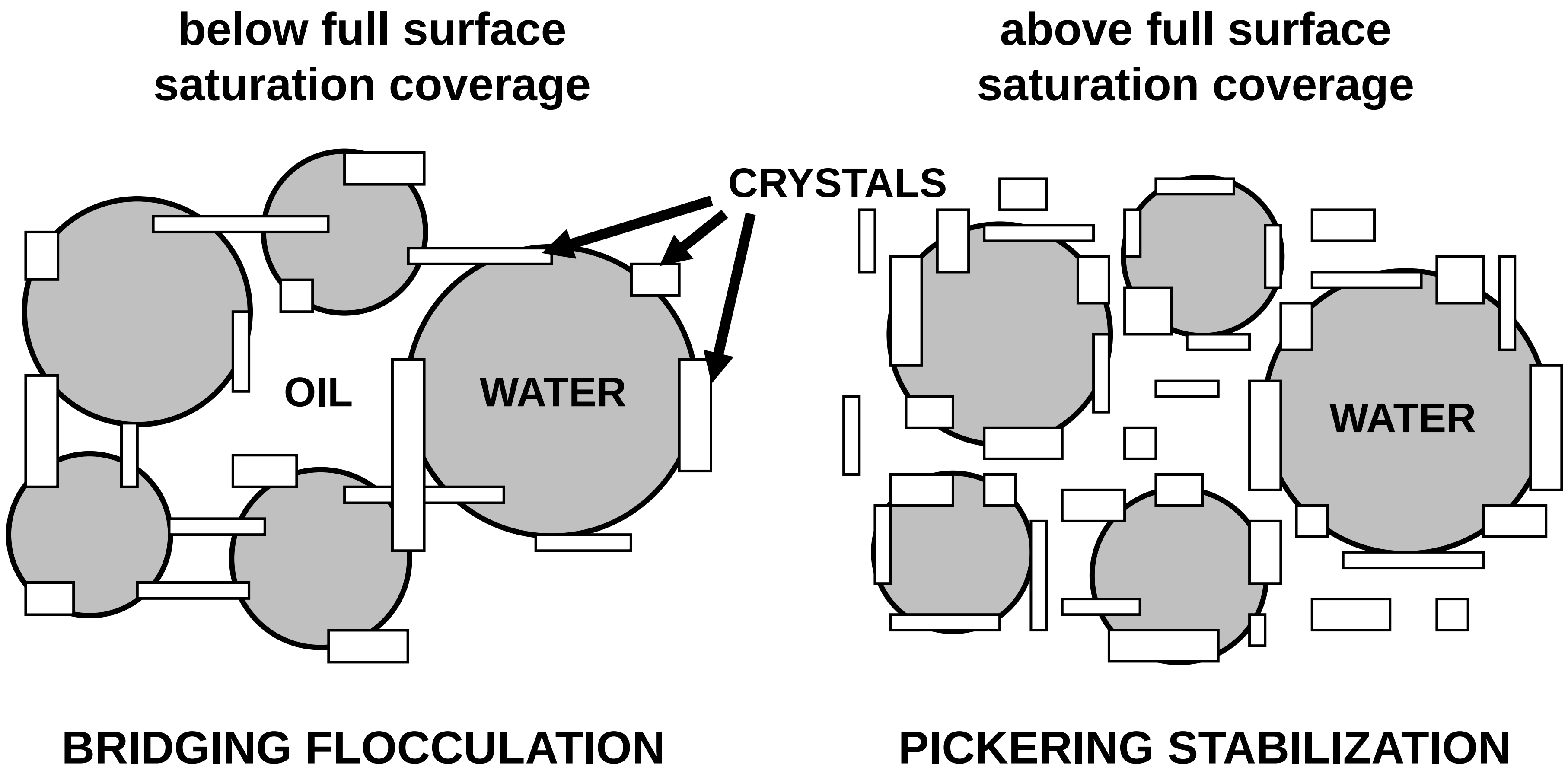
In butter and margarine, the fat crystals also interact and aggregate to form a three-dimensional network

$\Rightarrow$ **long-term stability to dispersed water droplets**

$\Rightarrow$ **solid-like ("spreadable") texture to the food product**

Effect of distribution of fat crystals on stability of water droplets dispersed in oil

FAT CRYSTAL CONCENTRATION



Wetting properties of fat crystals are affected by adsorption of emulsifiers at crystal surfaces

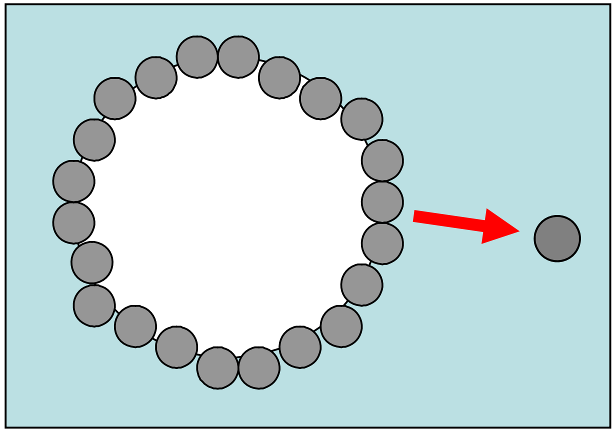
Consider a three-phase system of hardened palm oil (solid) + soybean oil (liquid) + water + emulsifier added to fat phase

No emulsifier → θ = 150°

Emulsifier	***Concentration***	**Contact angle (θ)** 1%
Saturated monoglyceride		**146**
Partly saturated monoglyceride		**138**
Sorbitan monooleate (Span 80)		**142**
Soybean lecithin		**132**

Campbell, 1989

Work to remove adsorbed particle from interface



For sphere of radius *r* at air–water (a–w) interface, free energy of spontaneous particle desorption is

$$\Delta G_d = G(\theta) - G(0)$$
$$= \pi r^2 \gamma_{aw} (1 - \cos\theta)^2$$

Let us assume
γ_{aw} = 50 mN m^{-1}
and θ = 45°

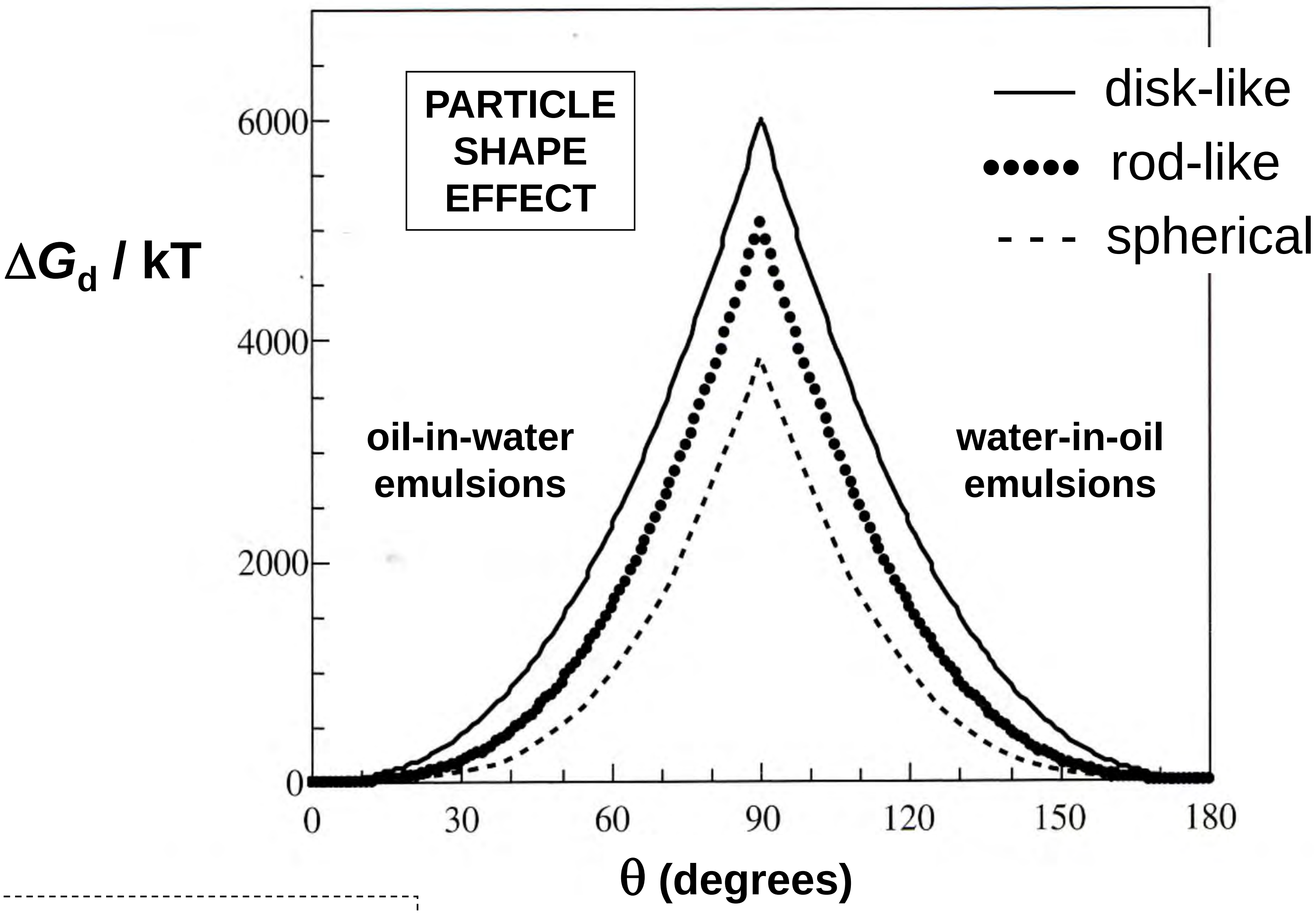
Predicted desorption free energy is

8×10^3 kT for 100 nm diameter sphere

80 kT for 10 nm diameter sphere

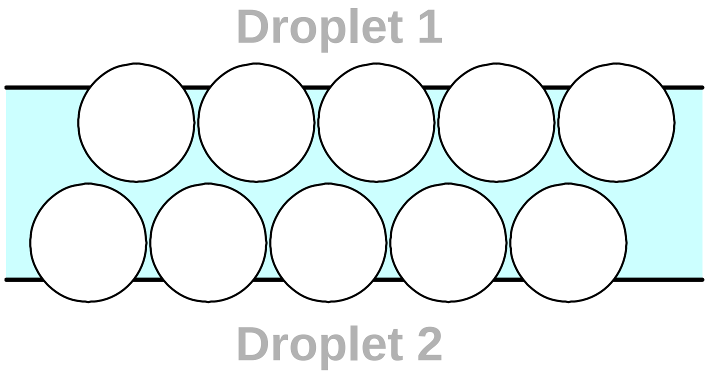
➔ **IRREVERSIBLE ADSORPTION** **(except for $\theta \rightarrow 0°$ or $\theta \rightarrow 180°$)**

Free energy of particle detachment *versus* contact angle θ

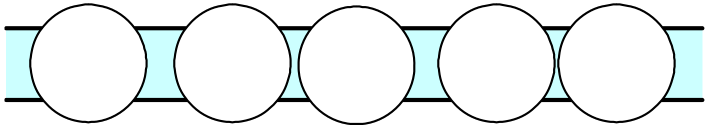


Binks & Horozov, 2006

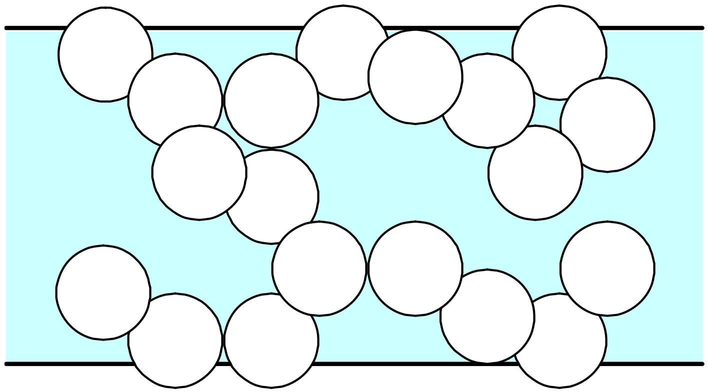
Interdroplet stabilizing particle structures



Two close-packed monolayers

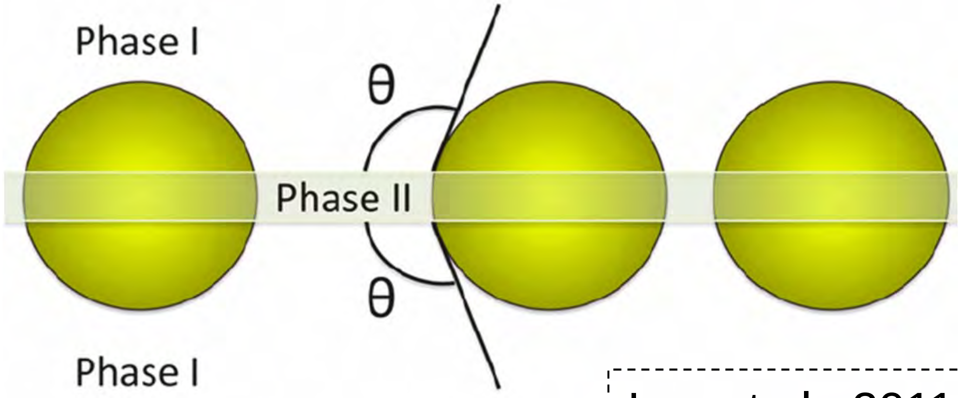


Single thin layer of bridging particles



Wider low-density region of aggregated particles

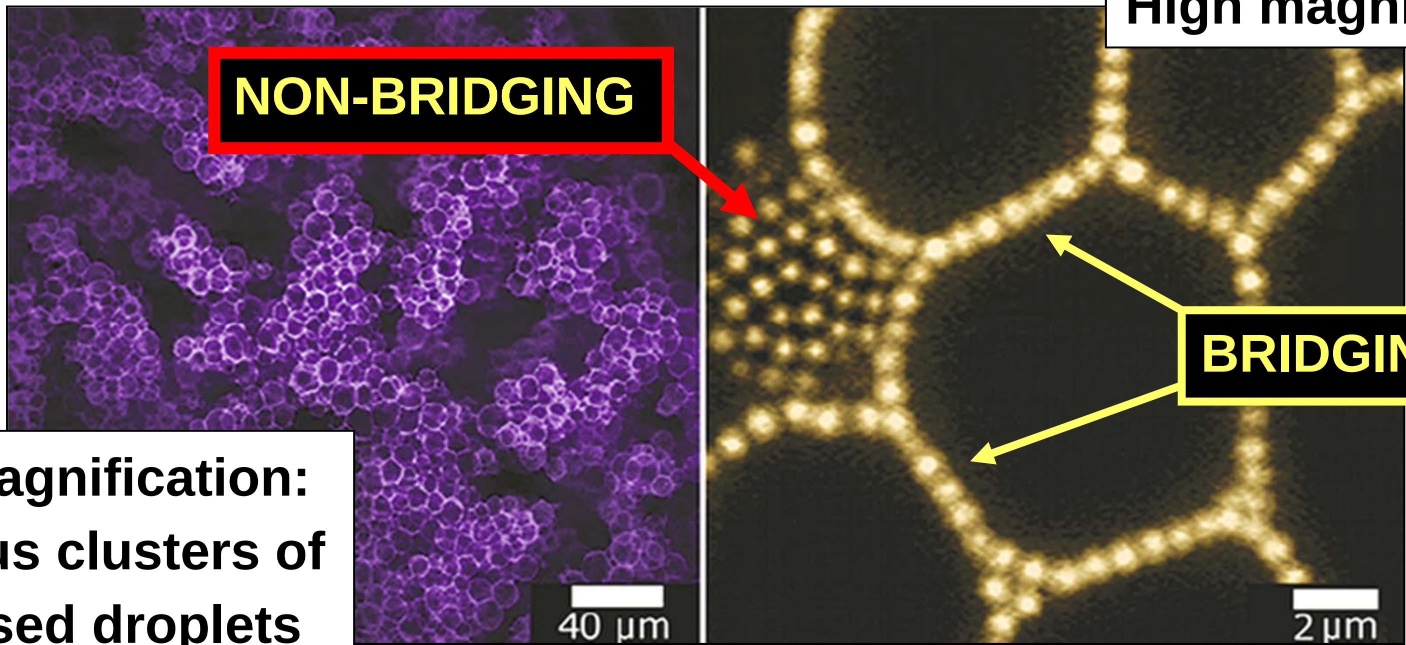
BRIDGING PARTICLE:
Equilibrium contact angle θ realized on both sides



Silica particles (1 μm)

Lee et al., 2011

Pickering Emulsion Gel formed by Droplet Bridging

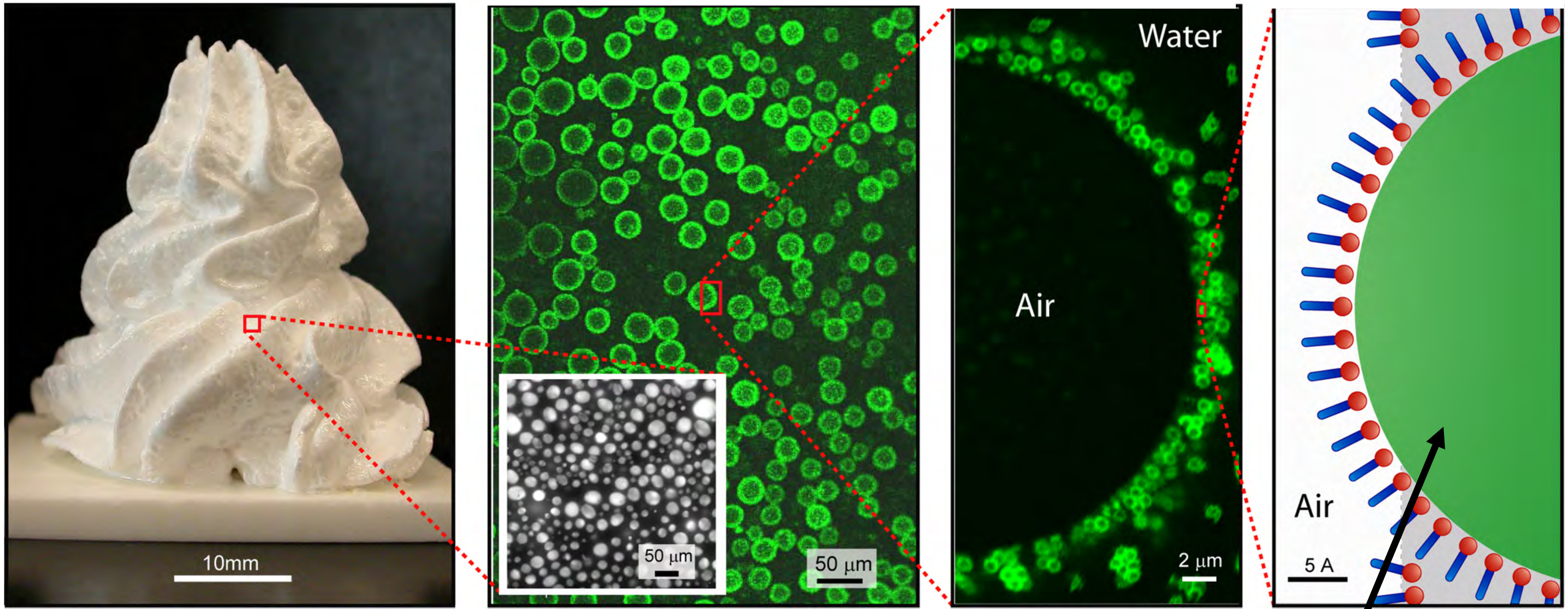


High magnification

Low magnification: tortuous clusters of dispersed droplets

Structuring of a particle-stabilized foam

MACROSCOPIC | **LOW-RESOLUTION MICROSCOPIC** | **HIGH-RESOLUTION MICROSCOPIC** | **NANOSCALE & MOLECULAR MODEL**



"Whipped cream-like" texture/rheology

Particle-stabilized bubbles

Gonzenbach et al., 2006

Silica microparticles stabilized by hexylamine as surfactant

What kinds of food-grade particles are available to stabilize oil-in-water emulsions (and foams) ?

MICROPARTICLES

Spray-dried soy protein particles (Paunov et al., 2007)

Hydrophobically modified starch particles (Yusoff & Murray, 2011)

Natural spore particles (Binks et al., 2005, 2011)

NANOPARTICLES

Cellulose nanocrystals (Kalashnikova et al., 2011)

Flavonoid (tiliroside) particles (Luo et al., 2011, 2012)

Chitin nanocrystals (Tzoumaki et al., 2011)

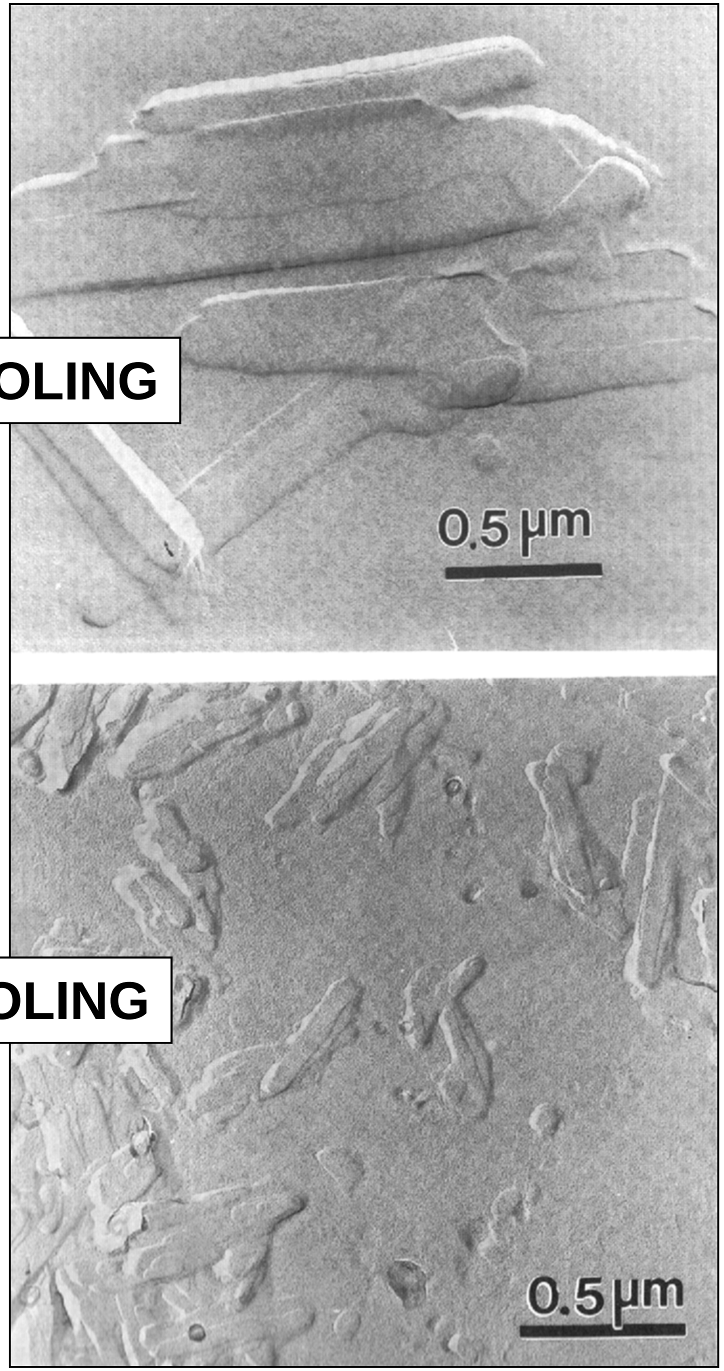
Ethyl cellulose particles (Jin et al., 2012)

Chemically modified starch nanospheres (Tan et al., 2012)

Corn protein (zein) particles (de Folter et al., 2012)

Solid lipid particles (Gupta & Rousseau, 2012)

Particle size may be determined by processing conditions



Electron micrographs of fat crystals in liquid fat blend

Heertje & Pâques, 2006

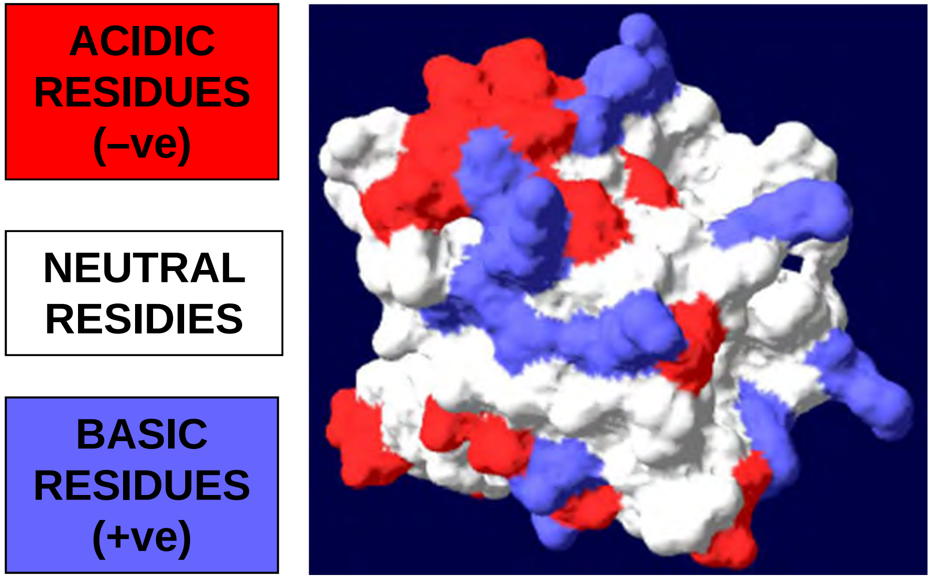
Is it reasonable to regard an individual protein molecule as a nanoparticle?

Globular protein molecules are typically **more deformable** than, say, silica nanoparticles.

And they **unfold** on adsorption at liquid interfaces.

Protein **aggregates** also become dissociated following adsorption.

β-lactoglobulin (~3 nm)



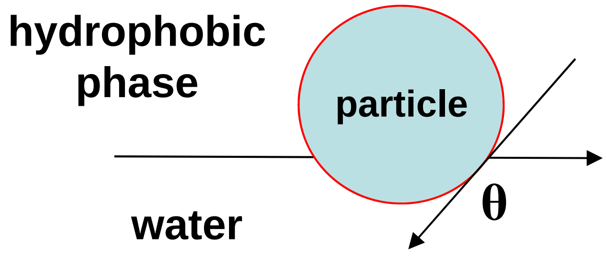
ADSORBED PROTEIN LAYERS → VISCOELASTIC and FLEXIBLE

ADSORBED PARTICLE LAYERS (close-packed) → HIGHLY RIGID

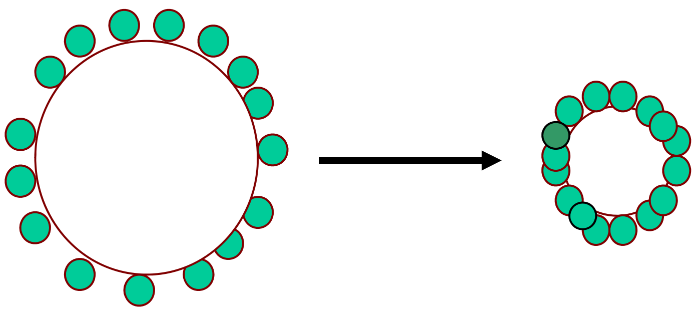
On this basis adsorbed food proteins do NOT possess typical Pickering stabilization characteristics

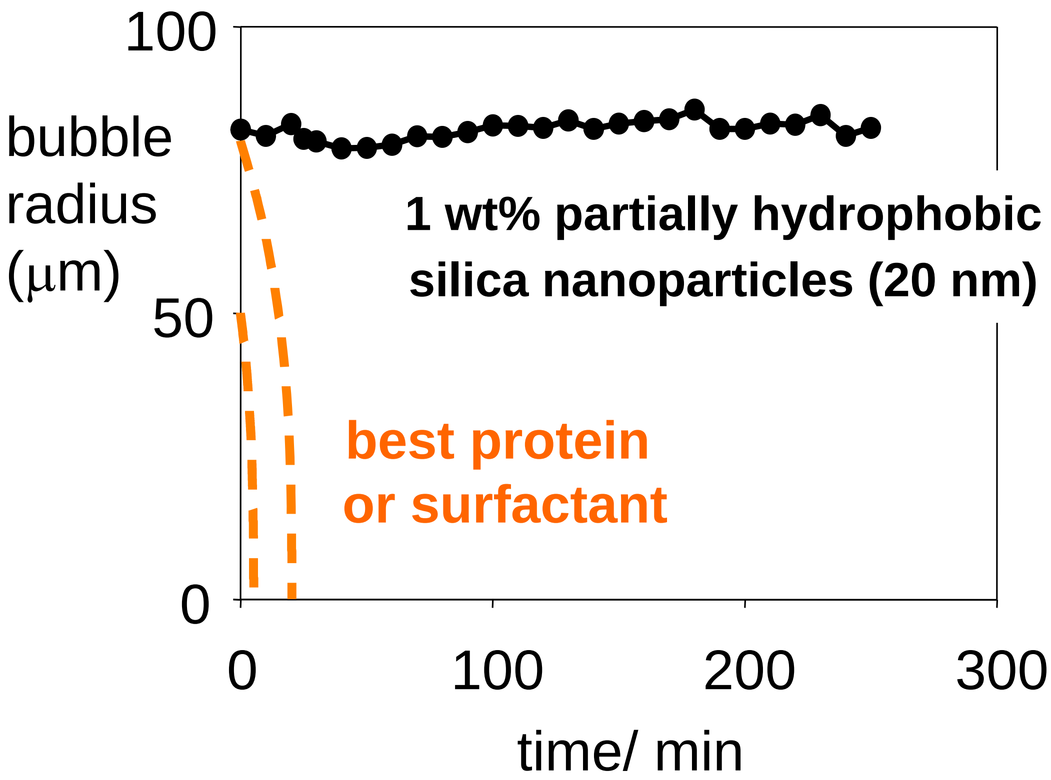
Advantages of particles

Excellent droplet / bubble stability



Stability to disproportionation





Dickinson et al., 2004

Two mechanisms of particle stabilization

- **Formation of <u>adsorbed particle layer</u>: Pickering stabilization**
  $\Rightarrow$ protects against coalescence and (possibly) flocculation

- **Immobilization of droplets in <u>aggregated particle network</u>**
  $\Rightarrow$ protects against coalescence and creaming/sedimentation

Which individual mechanism is most effective ?

Do both mechanisms operate together ?

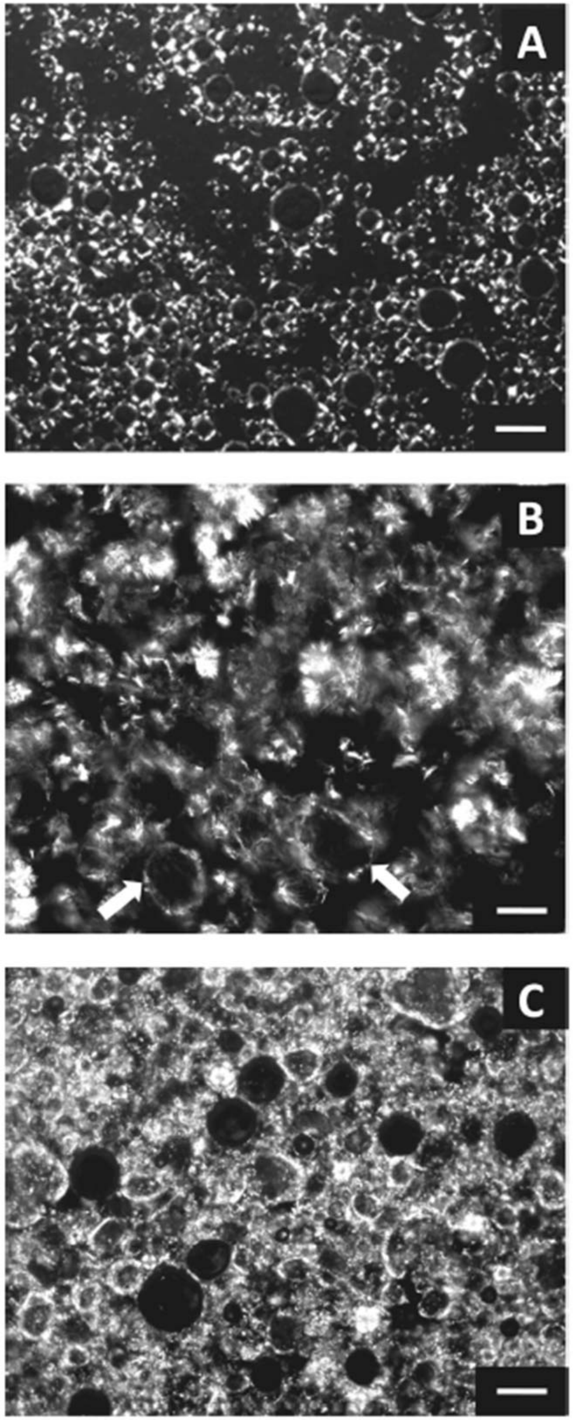
Stabilization of water-in-oil emulsions by fat crystals

80 wt% canola oil

$d_{33} \sim 20\ \mu m$

Rapid cooling (70 °C ➔ 20 °C) with continuous stirring

Ghosh et al., 2011



PICKERING STABILIZATION by monoglyceride crystals (GMS)

NETWORK STABILIZATION by triglyceride crystals (tristearin)

PICKERING/NETWORK STABILIZATION by monoglyceride + triglyceride crystals

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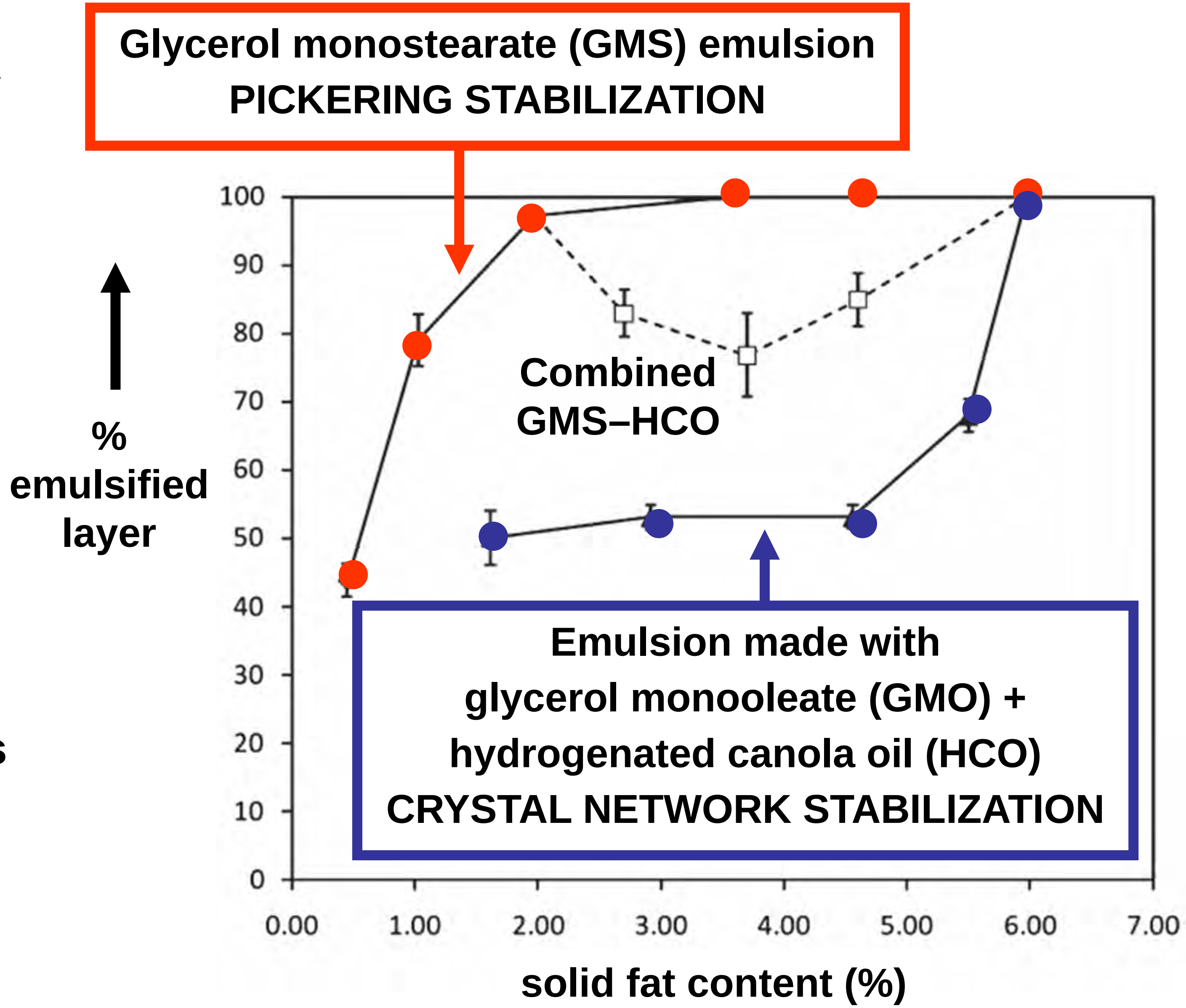
Ghosh et al., 2011

SEDIMENTATION STABILITY (7 days storage)



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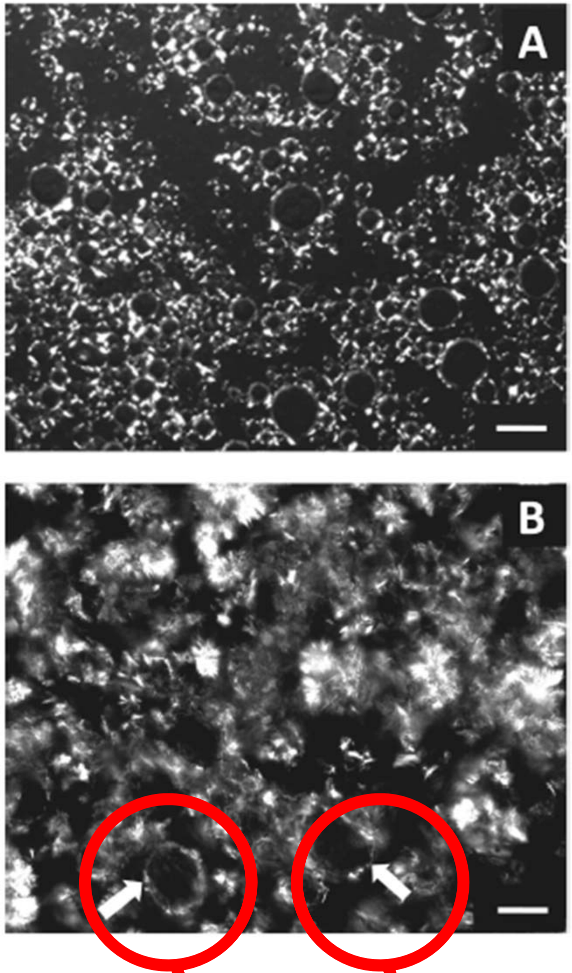

PICKERING STABILIZATION
by monoglyceride crystals (GMS)

NETWORK STABILIZATION
by triglyceride crystals (tristearin)

Wetting properties of crystals are affected by adsorption of GMO emulsifier at triglyceride crystal surface

GMO + HCO emulsion shows presence of some triglyceride crystals at the GMO-stabilized droplet surface

Stabilization of water-in-oil emulsions by fat crystals

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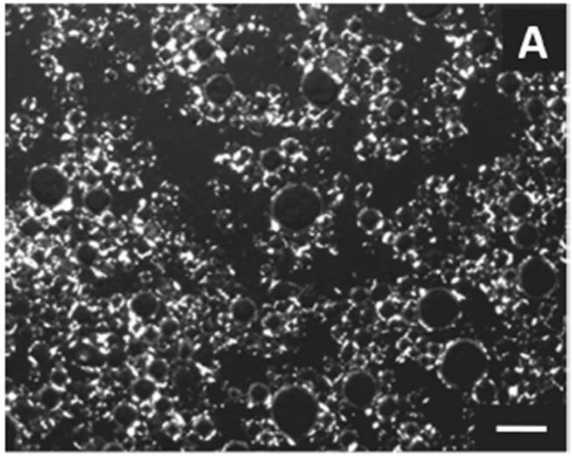
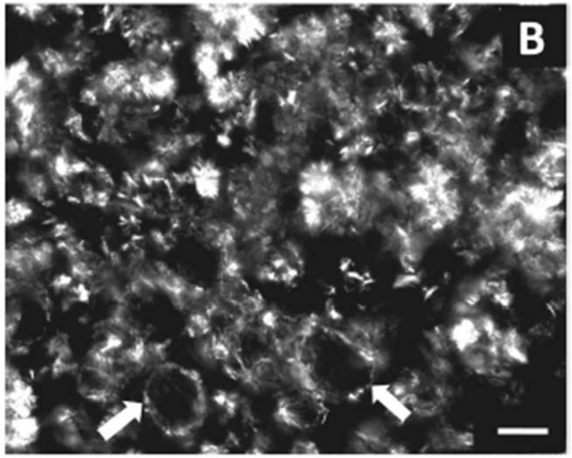




PICKERING STABILIZATION by monoglyceride crystals (GMS)

NETWORK STABILIZATION by triglyceride crystals (tristearin)

CONCLUSION ...

Pickering fat crystals are more effective than network fat crystals for W/O emulsion stabilization

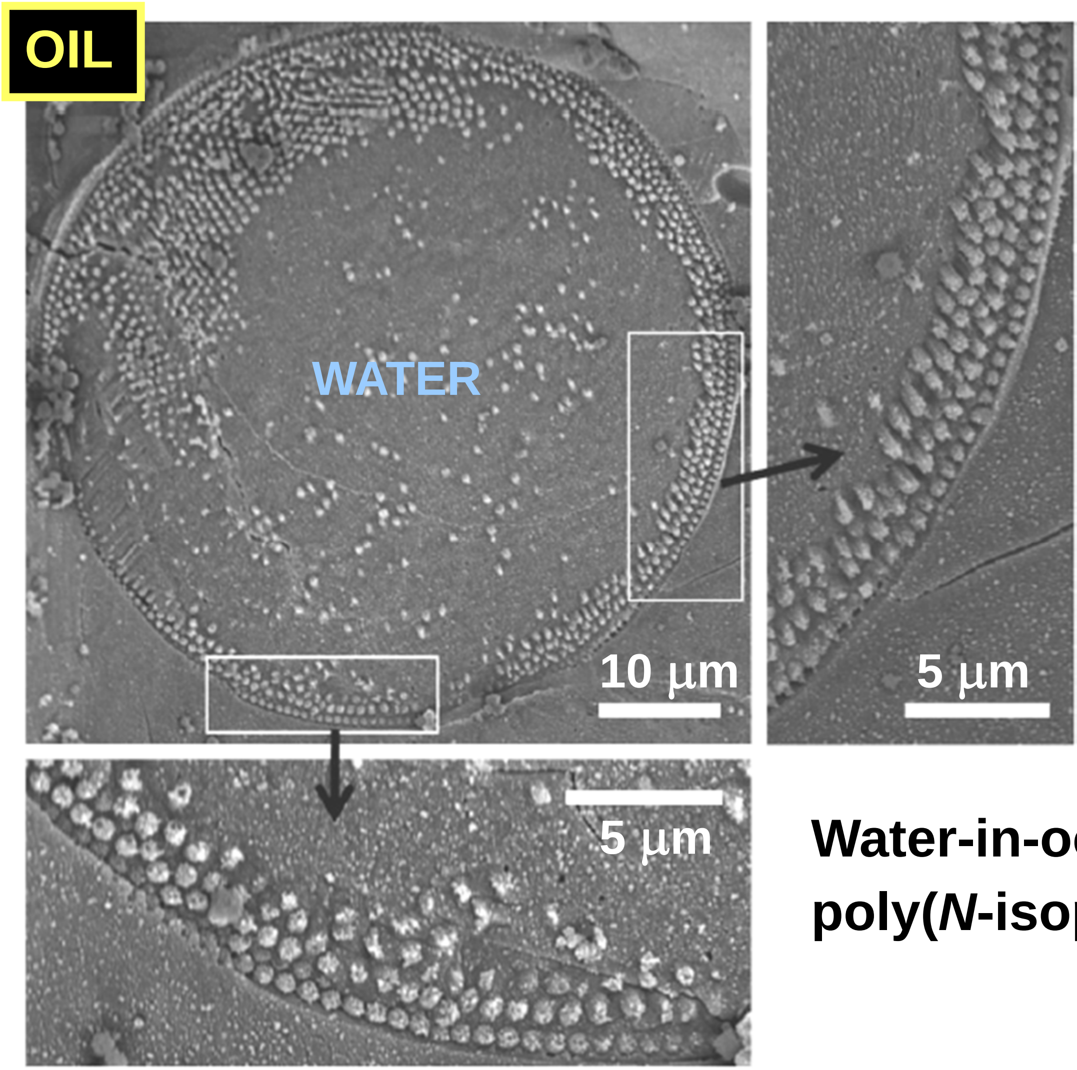
Are there viable alternatives to fat crystals as particle stabilizers of water-in-oil emulsions?

Main problem: food biopolymers are water-soluble or water-dispersible $\Rightarrow$ favour oil-in-water emulsions (Finkle's rule)

One possible solution: swollen polymer-based microgel particles that can self-assemble at the oil–water interface in more complex manner

Novel microparticles for stabilizing water-in-oil emulsions:

water-dispersible microgels



Interfacial structure characterized by microgel multilayers

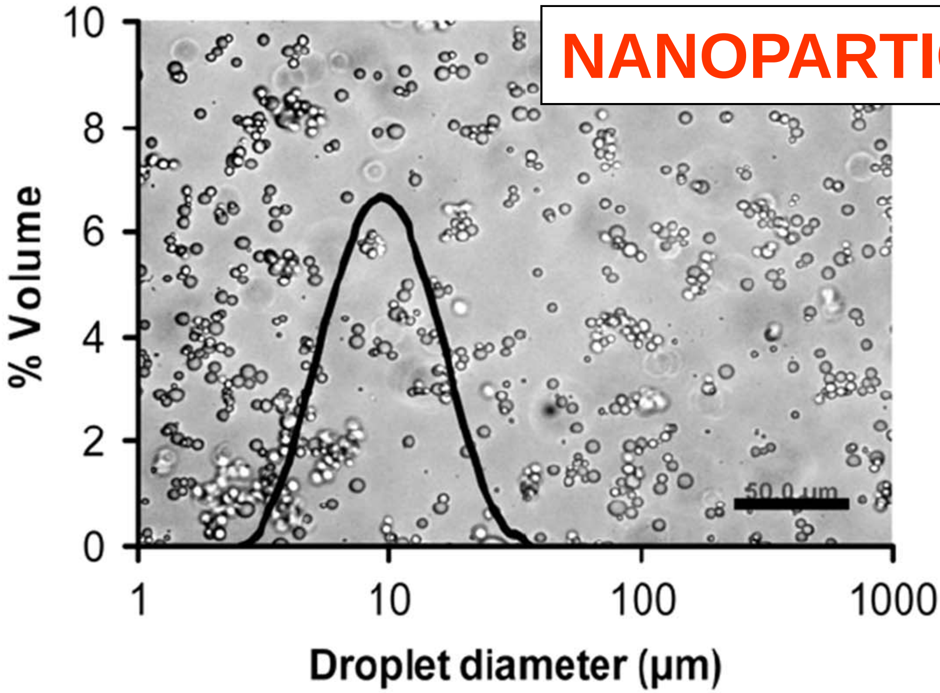
Structure in contradiction of Finkle's rule due to oil incorporation into the microgel particles

Water-in-octanol droplets stabilized by poly(*N*-isopropylacrylamide) microgels

Destribats et al., 2011

Examples of particle-stabilized oil-in-water emulsions

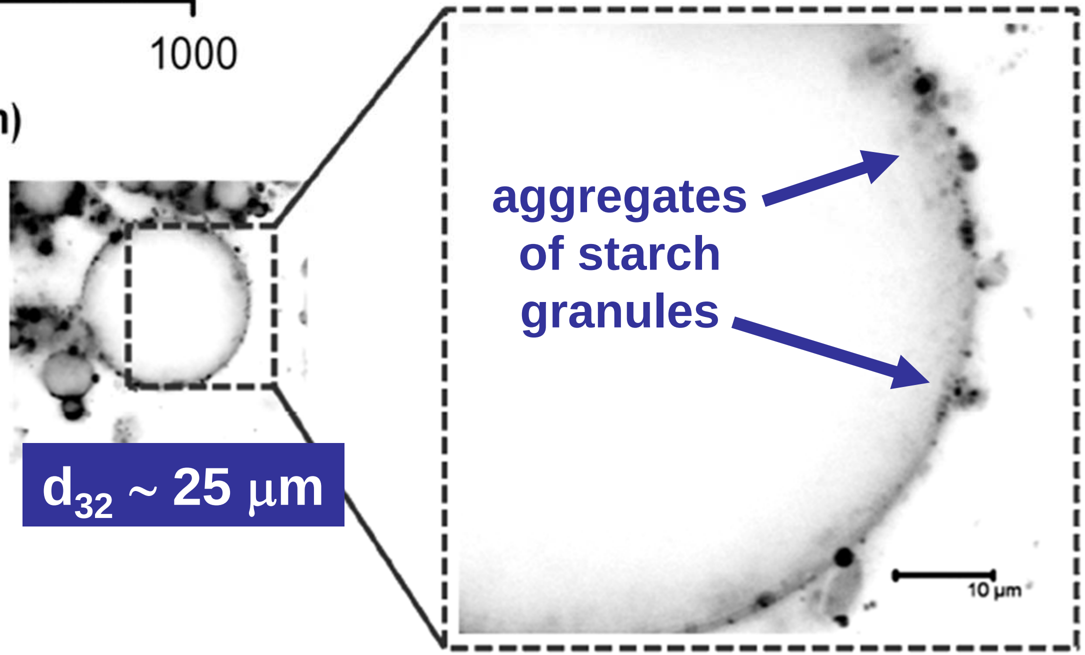
NANOPARTICLES



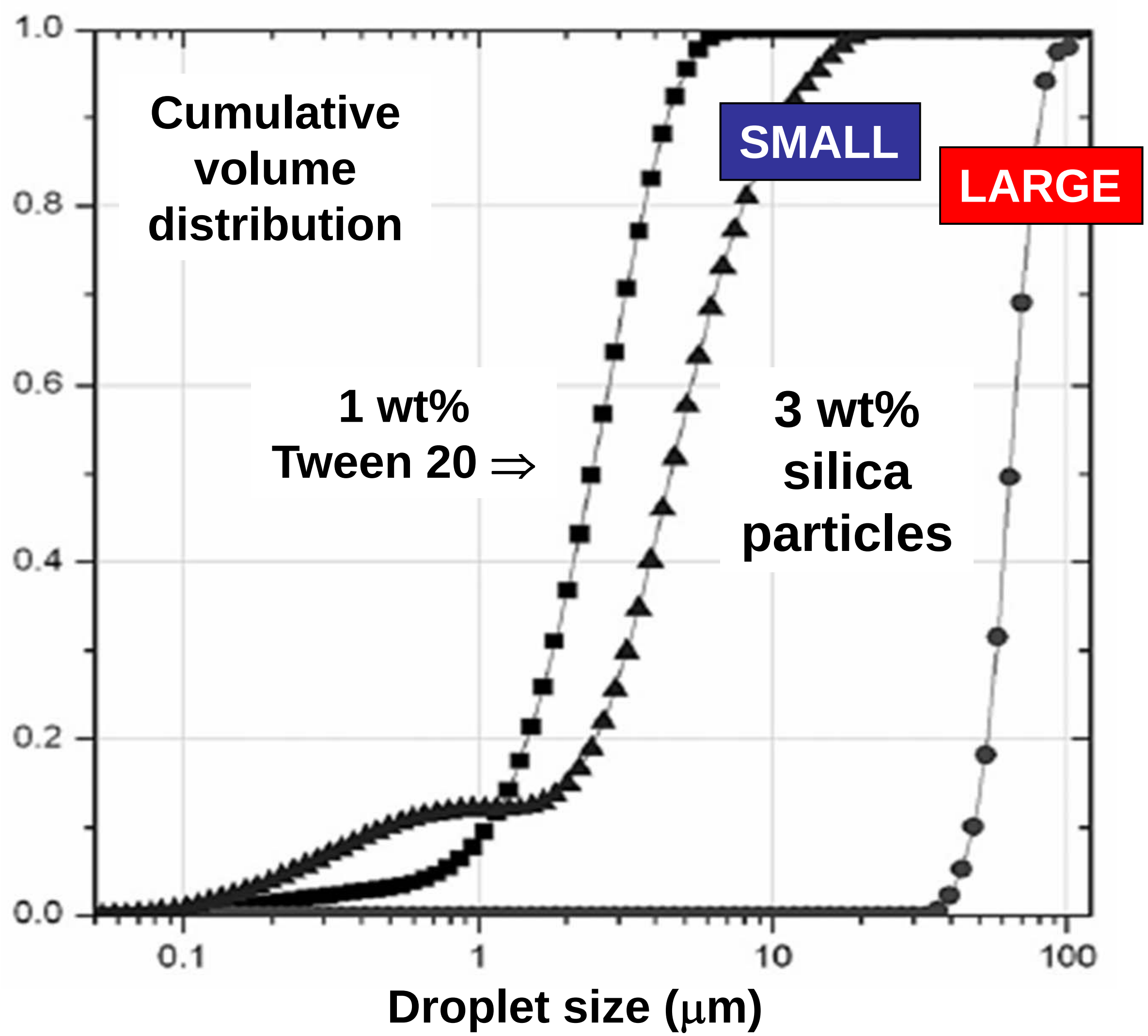
Oil droplets stabilized by chitin nanocrystals (240 nm × 20 nm) at pH = 3
(Tzoumaki et al., 2011)

MICROPARTICLES

Oil droplets stabilized by hydrophobically modified starch particles (~ 10 µm)
(Yusoff & Murray (2011)



Nanoparticles are generally required in order to prepare micrometre-sized Pickering emulsions



SILICA PARTICLES

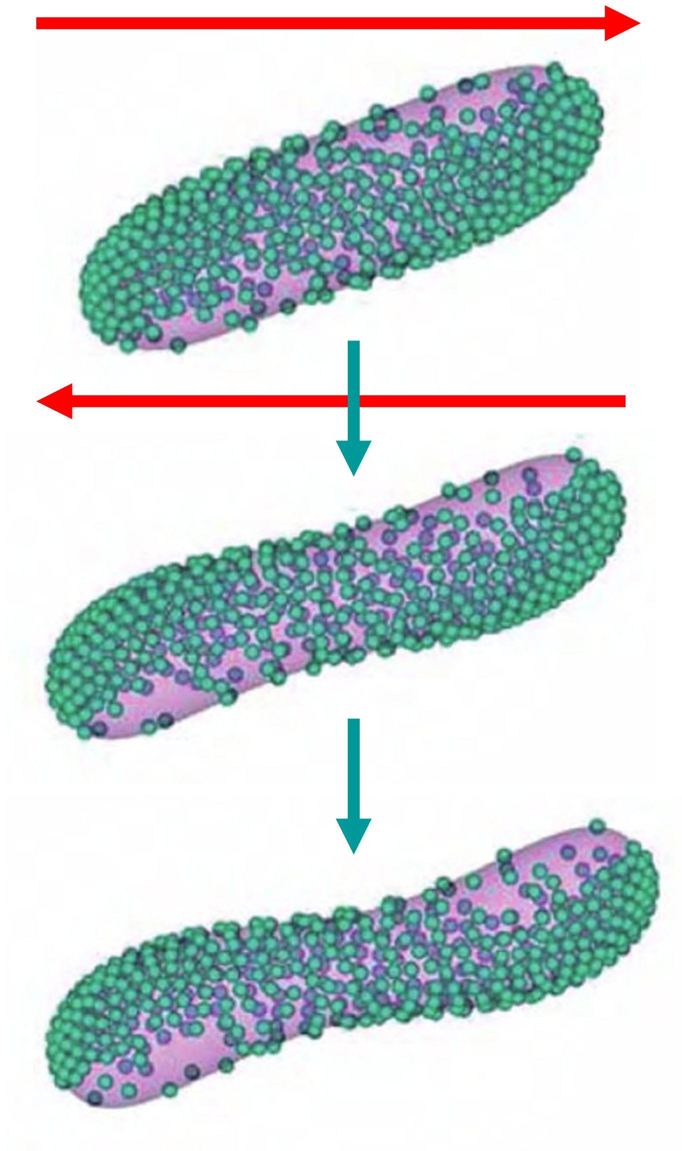
Small = 12 nm

Large = 200 nm

High-pressure homogenization (800 bar)

20 vol% triglyceride oil-in-water emulsions (pH = 2)

Köhler et al. (2010)



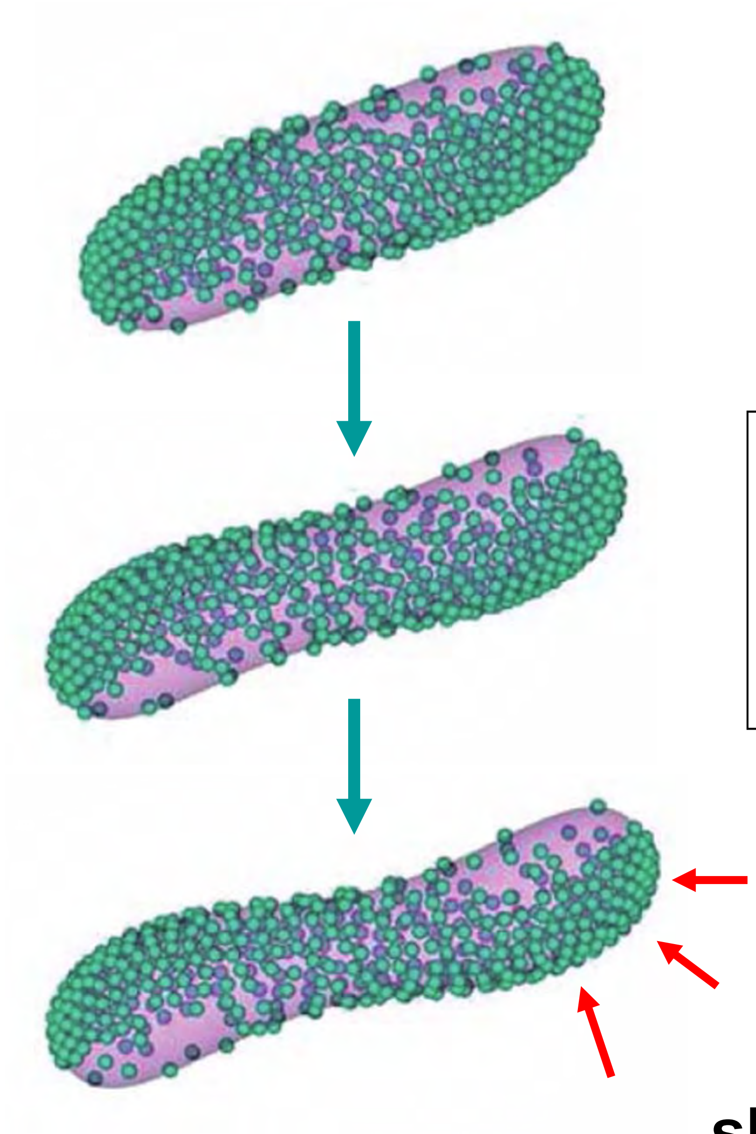
Particle-coated droplet in shear flow

Lattice Boltzmann simulation

55% coverage of nanoparticles at original oil–water interface

Frijters et al. (2012)

Particle-coated droplet in shear flow

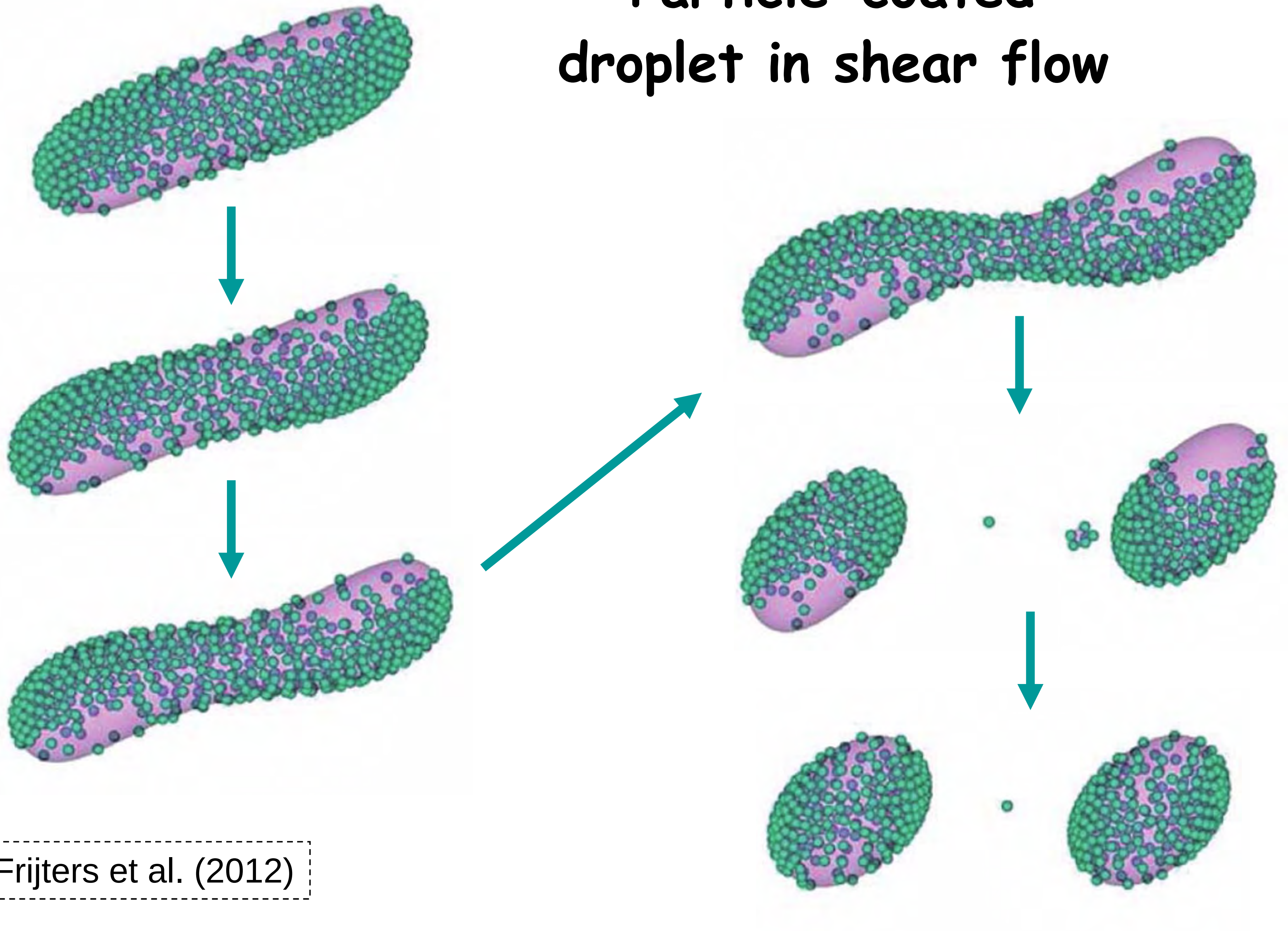


Particles not homogeneously distributed over droplet surface

Particles form more densely packed patches in areas of low shear velocities and high curvature

Frijters et al. (2012)

Particle-coated droplet in shear flow

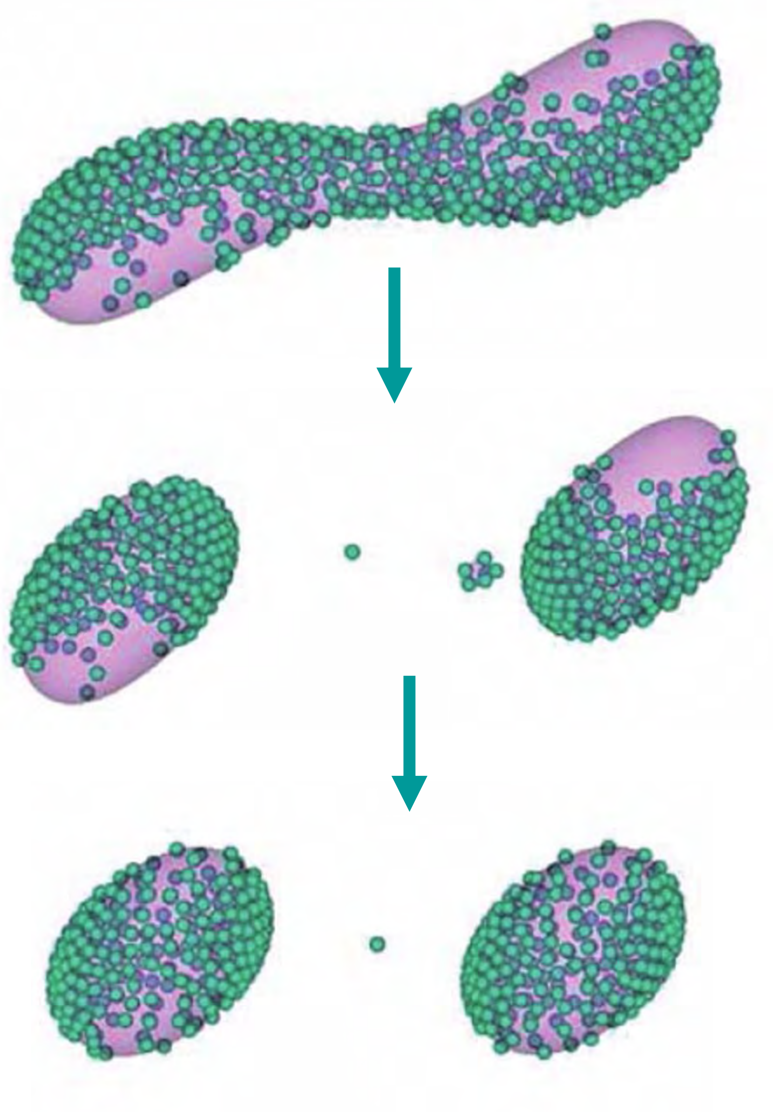


Frijters et al. (2012)

Particle-coated droplet in shear flow

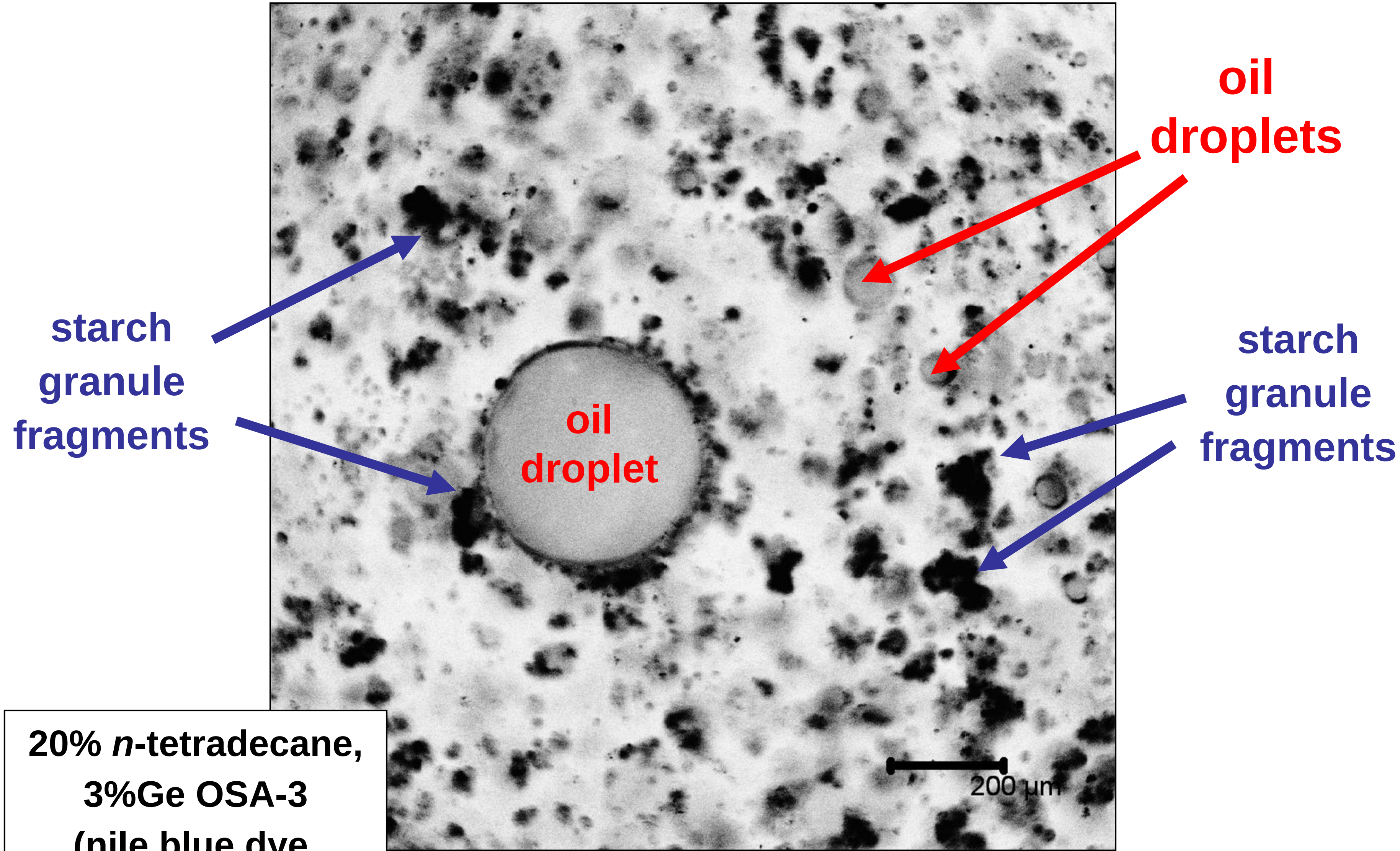
Particle presence induces a larger deformation at constant capillary number

Adsorbed particles cause droplets to break up more easily



Frijters et al. (2012)

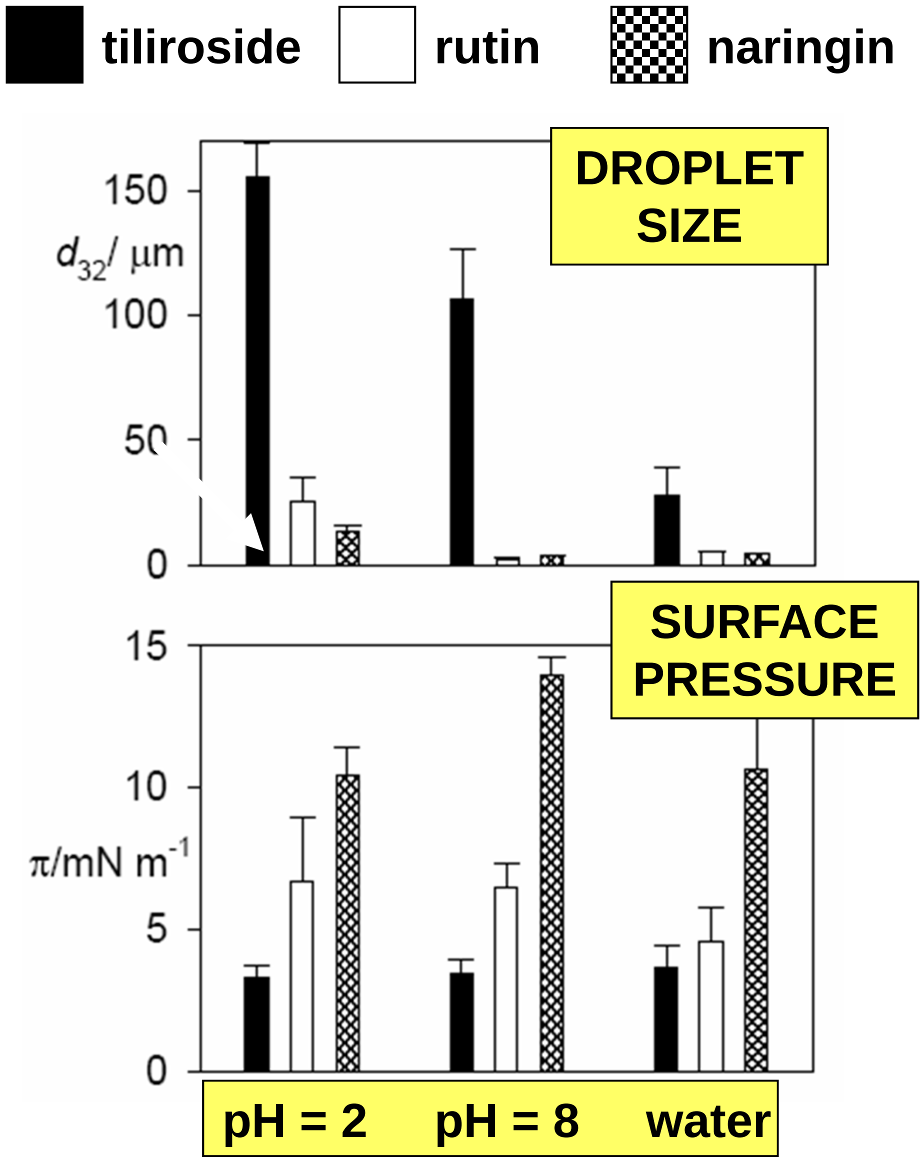
Oil-in-water emulsions stabilized by hydrophobic starch microparticles



20% *n*-tetradecane, 3%Ge OSA-3 (nile blue dye, 0.1% xanthan)

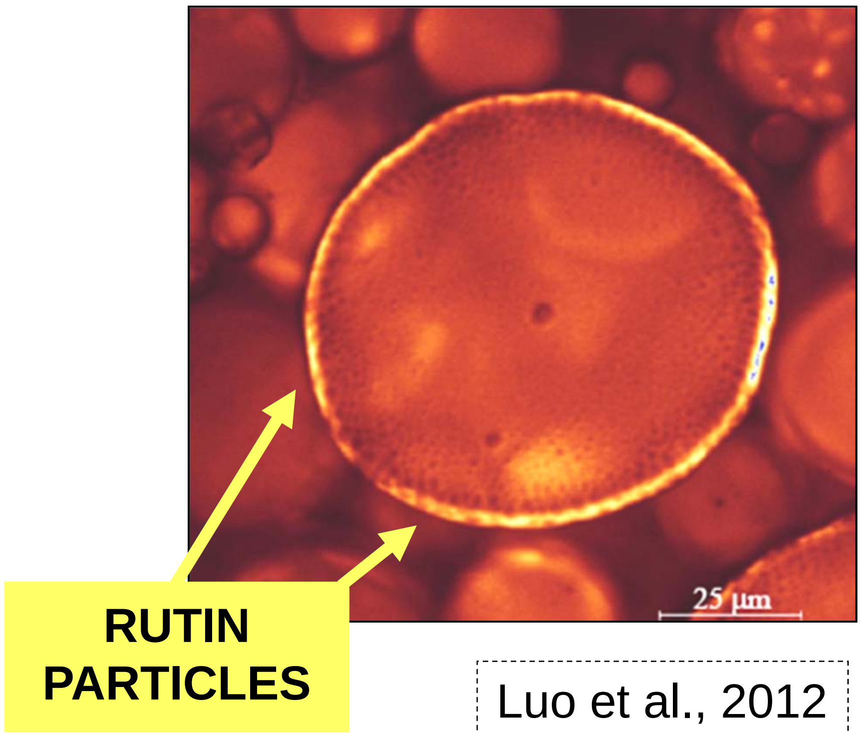
Yusoff & Murray, 2009

Oil-in-water emulsions stabilized by flavonoid particles



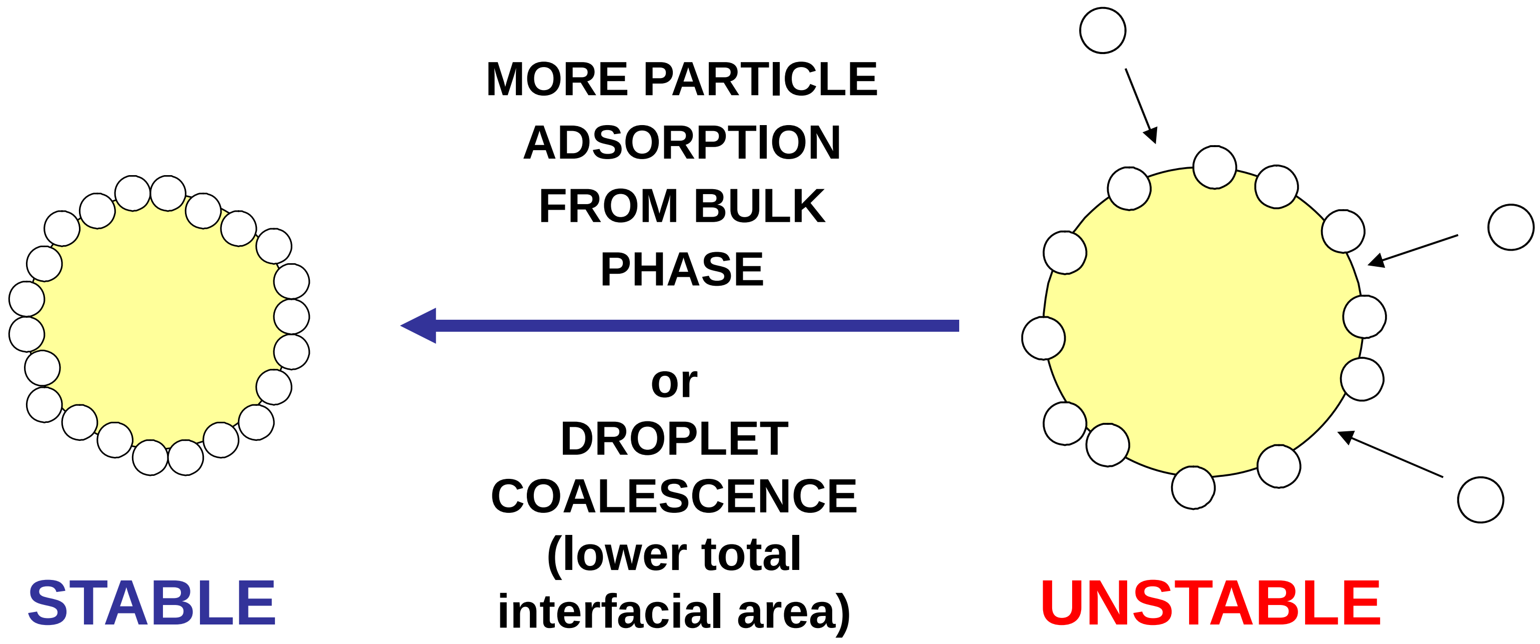
pH affects particle charge and flavonoid solubility

Emulsion made with buckwheat tea extract (rich in rutin)



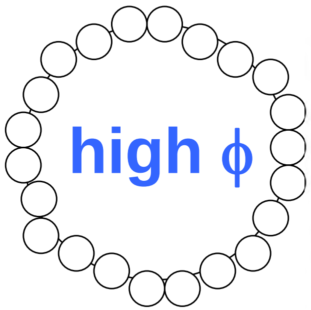
Luo et al., 2012

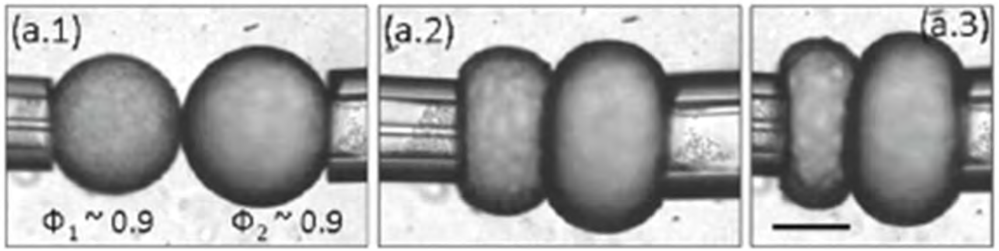
In absence of extensive particle aggregation in continuous phase, effective long-term Pickering stabilization requires **full coverage** of the oil–water interface by solid particles



Particle-stabilized bubbles: shrinkage of unstable bubbles due to gaseous diffusion through the continuous phase

Coalescence stability of particle-stabilized droplets

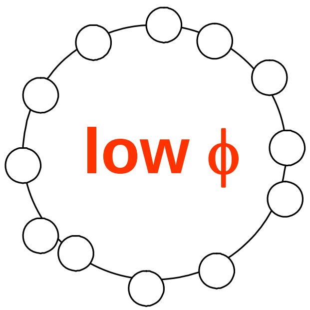


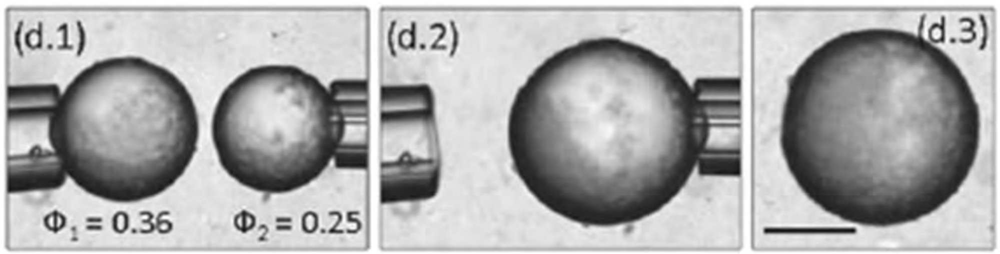


TOTAL STABILITY

Full surface coverage of silica particles (1.5 μm) at oil–water interface (contact angle 70°)

Low surface coverage of particles at interface





FULL COALESCENCE

Pawar et al., 2011

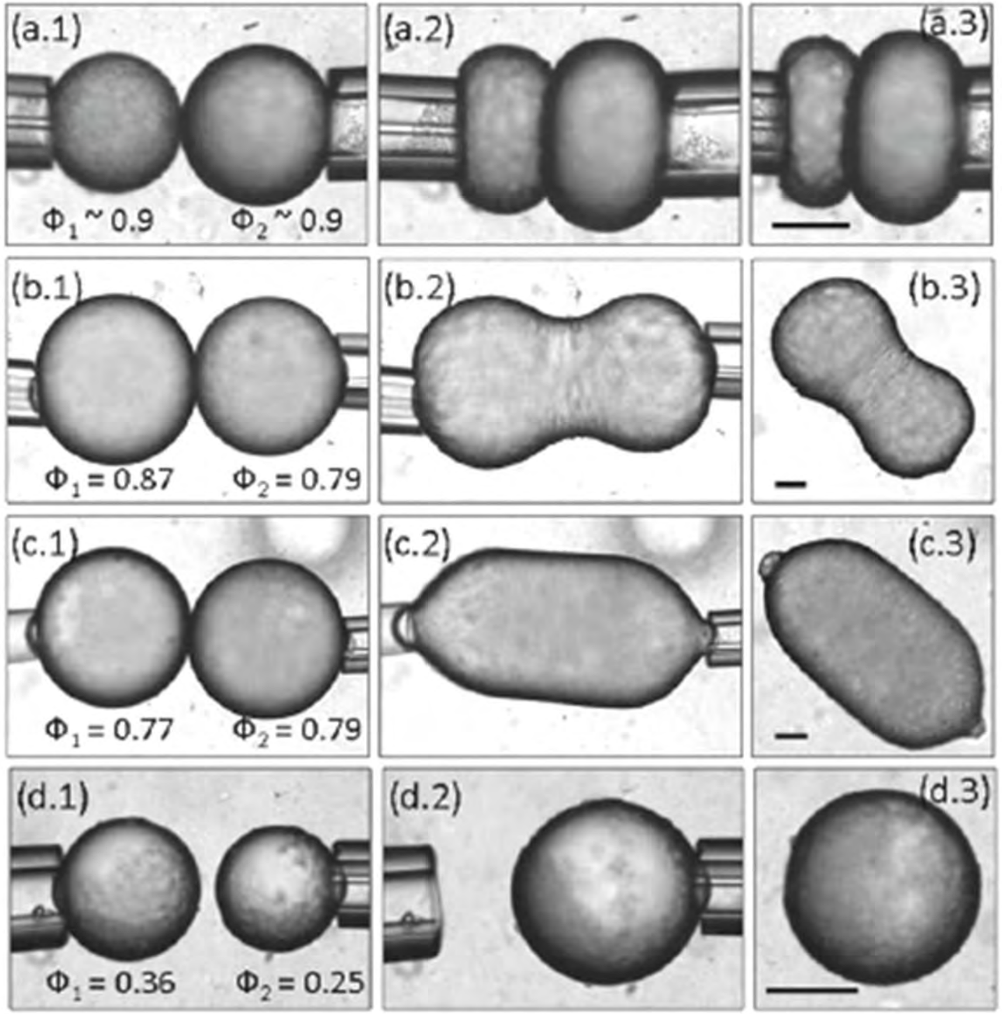
Scale bar ≡ 50 μm

Coalescence stability of particle-stabilized droplets

high ϕ

PARTICLE COVERAGE ON SURFACE

low ϕ



TOTAL STABILITY

ARRESTED COALESCENCE

FULL COALESCENCE

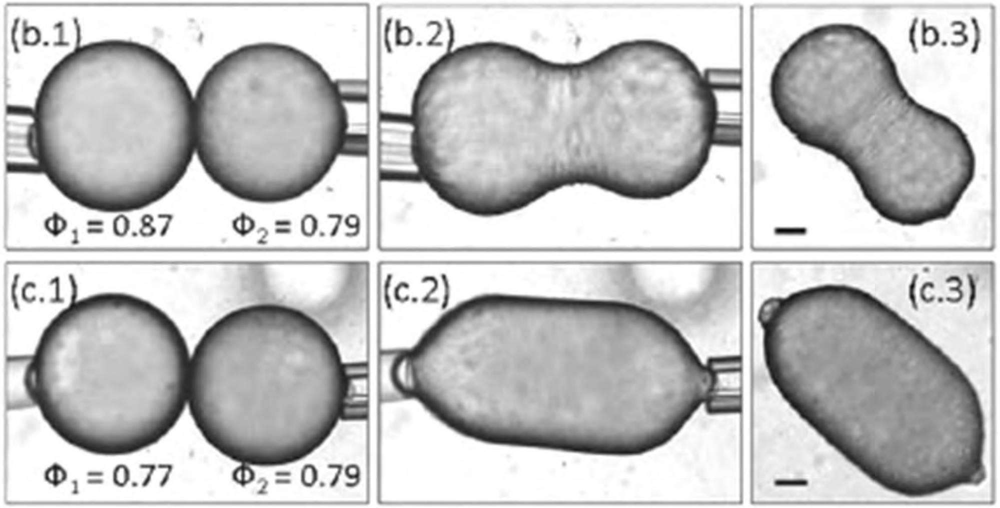
Pawar et al., 2011

Scale bar = 50 μm

Coalescence stability of particle-stabilized droplets

Due to the interfacial rigidity of close-packed adsorbed layers, Pickering emulsions may contain non-spherical liquid droplets

Intermediate particle coverage



ARRESTED COALESCENCE

... a different phenomemon from "partial coalescence" of semi-crystalline fat droplets (e.g. in whipped cream)

Pawar et al., 2011

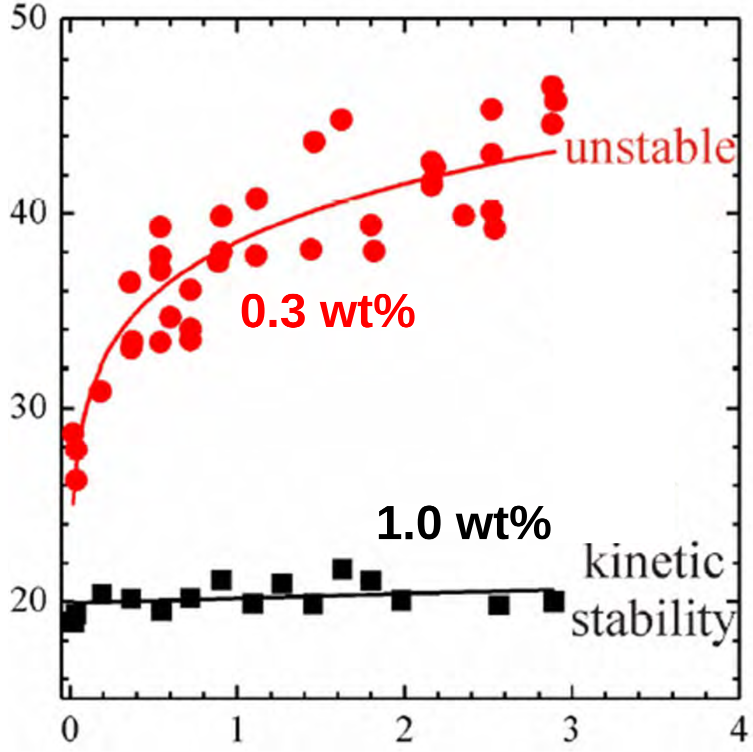
Scale bar ≡ 50 μm

Destabilization at low particle concentrations

Emulsion stability increases with particle concentration C_p

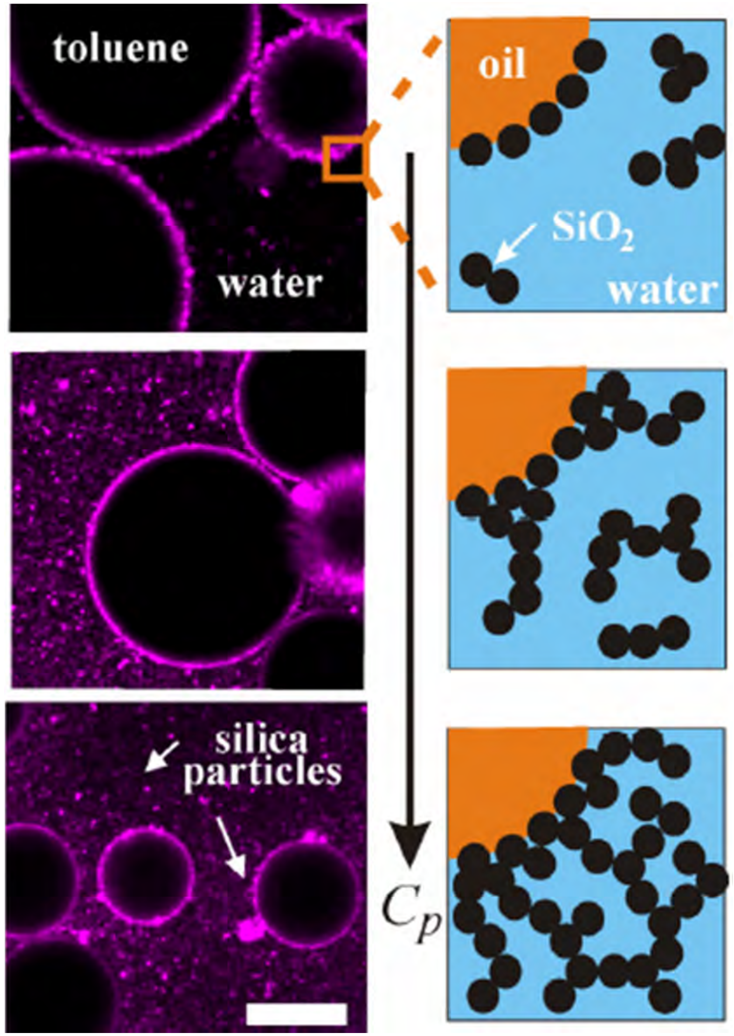
10 vol % toluene-in-water emulsions stabilized by silica particles (10–30 nm)

Average droplet radius (μm)



Time (10^4 s)

Juarez & Whitby, 2012



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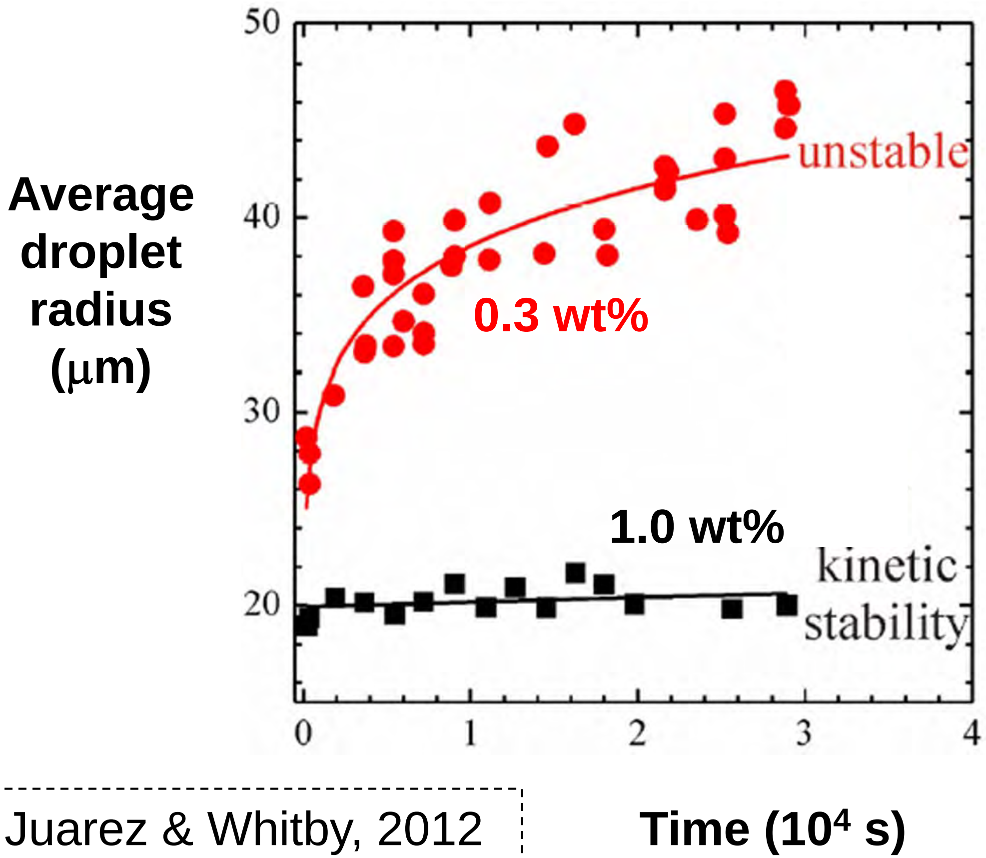
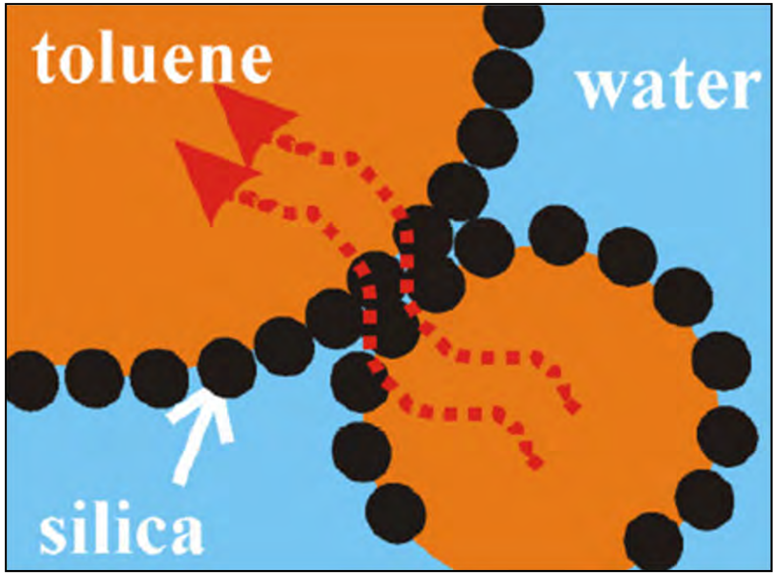


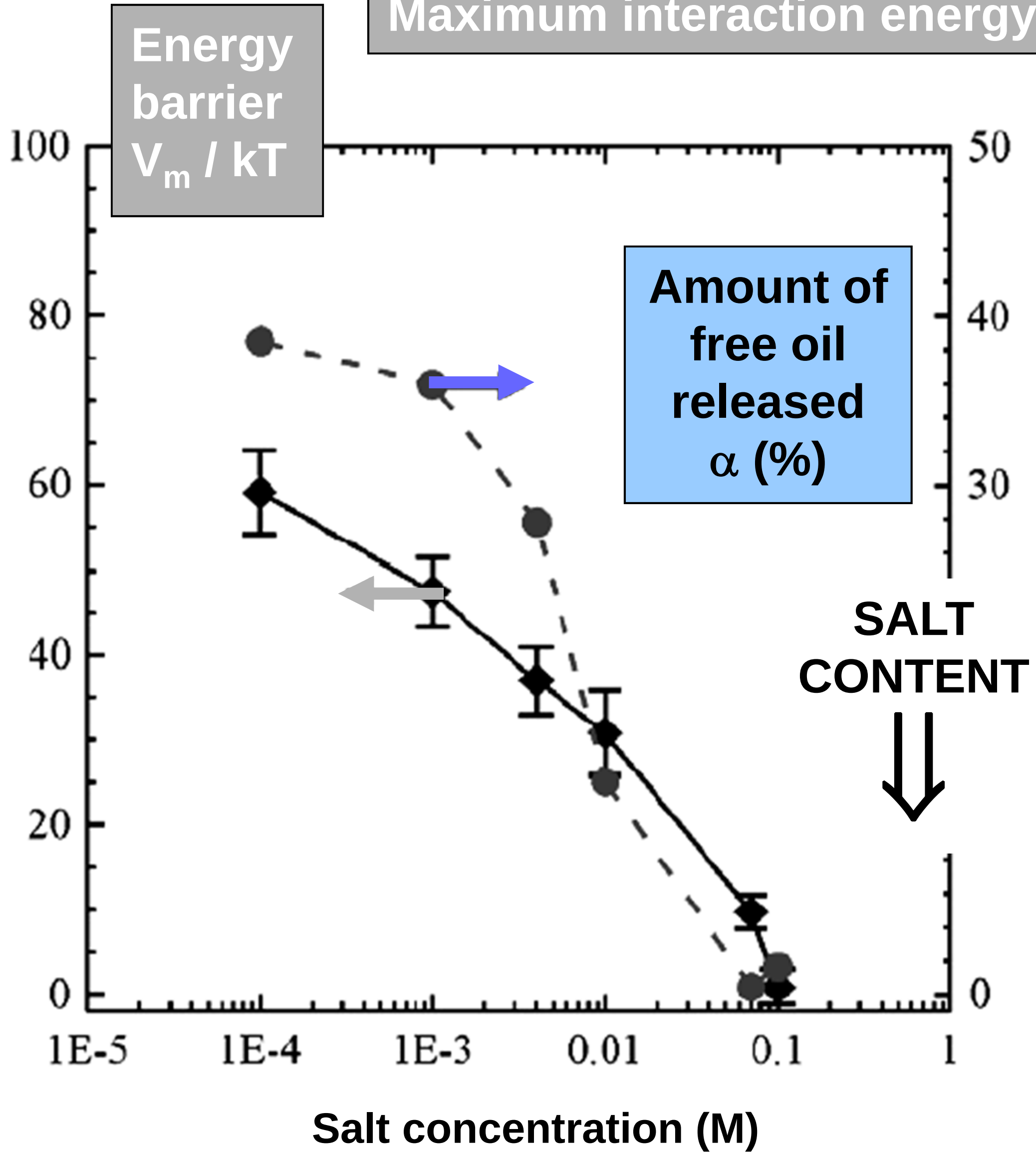
Juarez & Whitby, 2012

Destabilization mechanism involves transport of oil between flocculated droplets poorly stabilized by particles

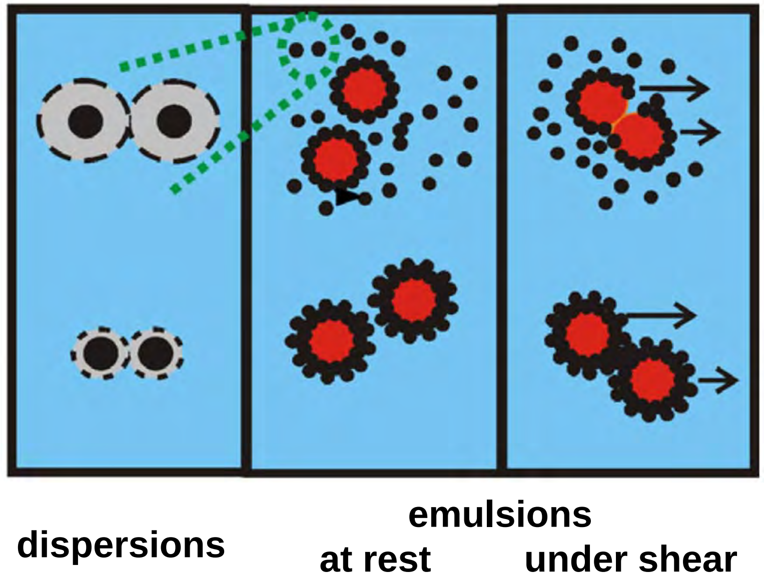


Shear-induced coalescence of particle-stabilized emulsions

Maximum interaction energy in calculated colloidal potential



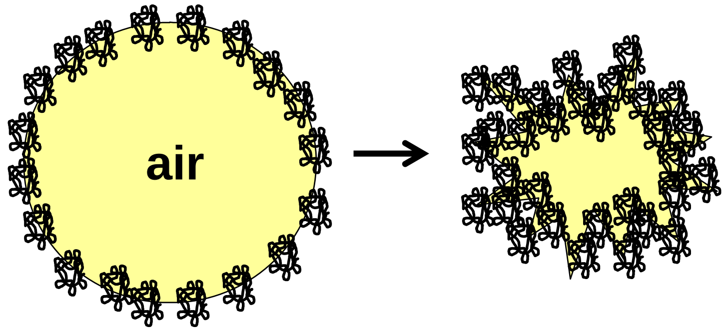
Oil-in-water emulsions
(50 vol% bromohexadecane,
2 wt% silica particles)
sheared at 10^3 s^{-1} for 1 min



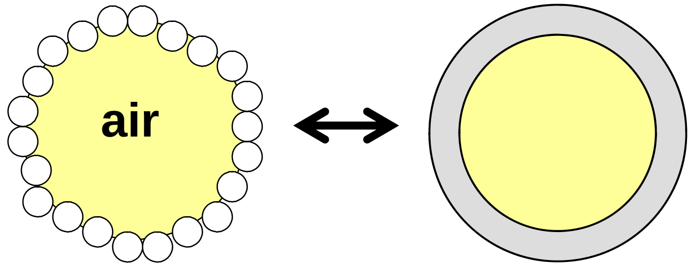
Whitby et al., 2011

At boundary of colloidal and molecular length scales lie <u>small nanoparticles</u> (and also protein molecules)

Viscoelastic protein monolayer cannot stabilize against bubble growth or shrinkage by disproportionation



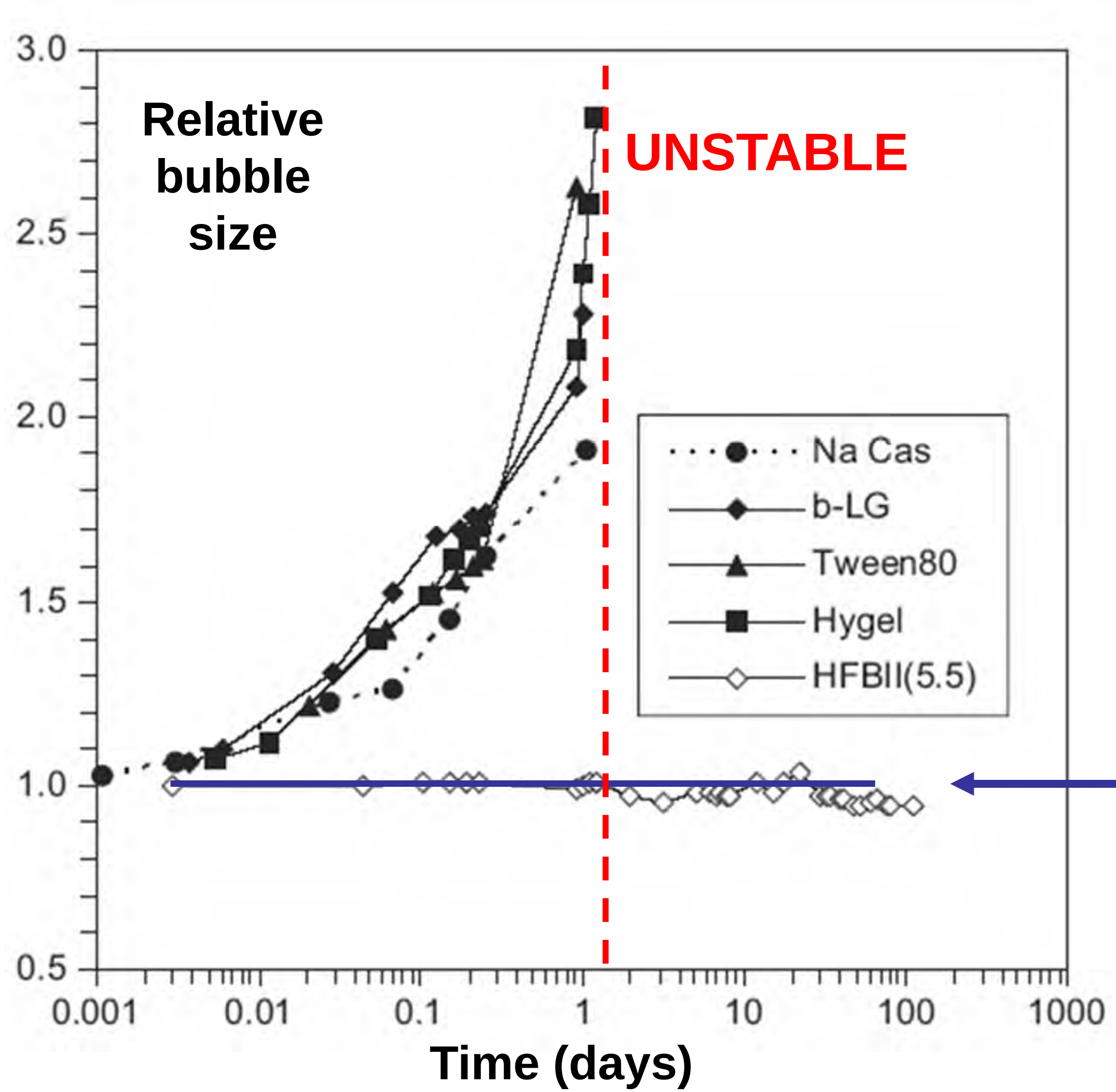
But rigid layer of solid particles can provide stability against disproportionation and coalescence



behaves like rigid shell

An unusual protein that behaves rather like a surface-active nanoparticle ... **hydrophobin**

Comparison of hydrophobin with some other food proteins and surfactants



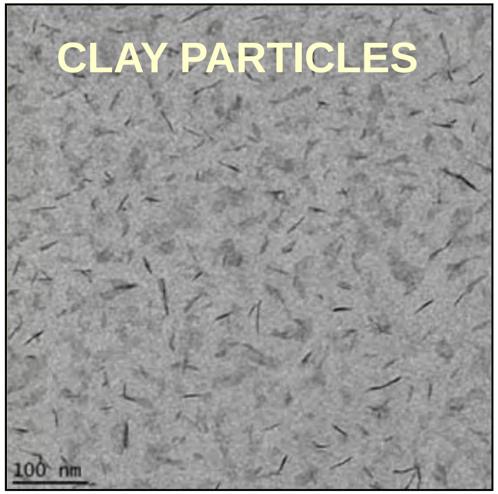
Bubble sizes for aqueous foams prepared with various surface-active agents

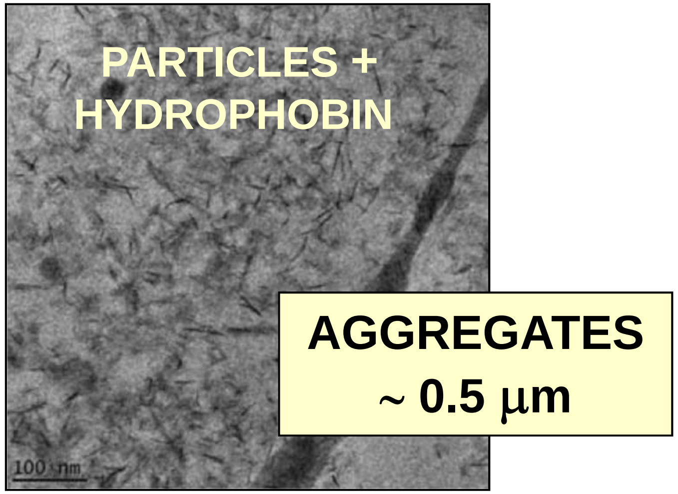
Hydrophobin foam stable for several months

Cox et al., 2009

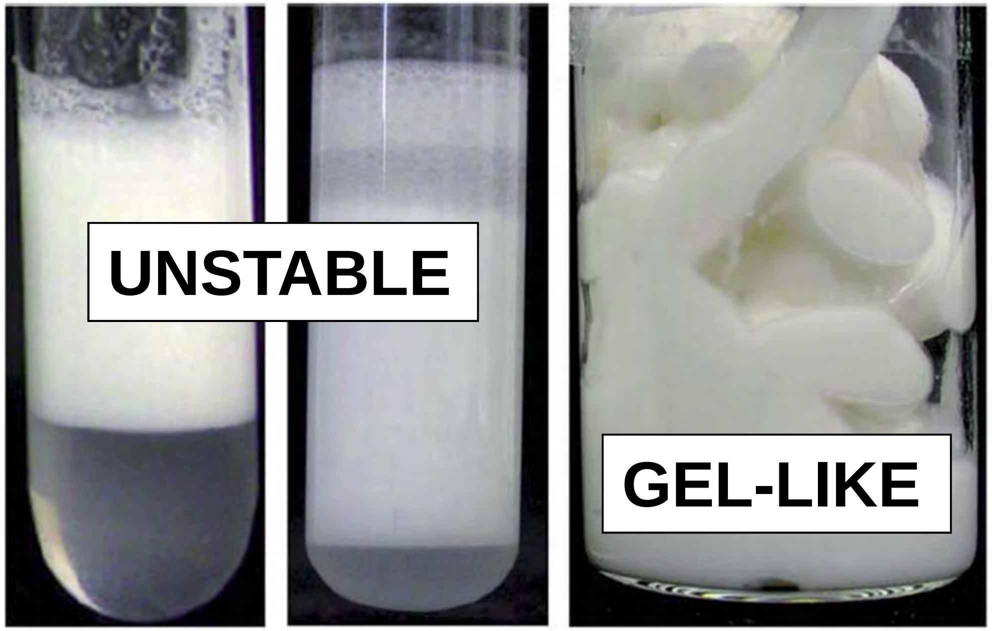
Stabilization by Mixture of Particles and Protein

Concentrated silicone oil-in-water emulsions (ϕ = 0.65) stabilized by clay Laponite platelets (10–50 nm) + hydrophobin (19 kDa, p*I* = 6.1)





One-day-old emulsions (homogenization at 10^3 bar)



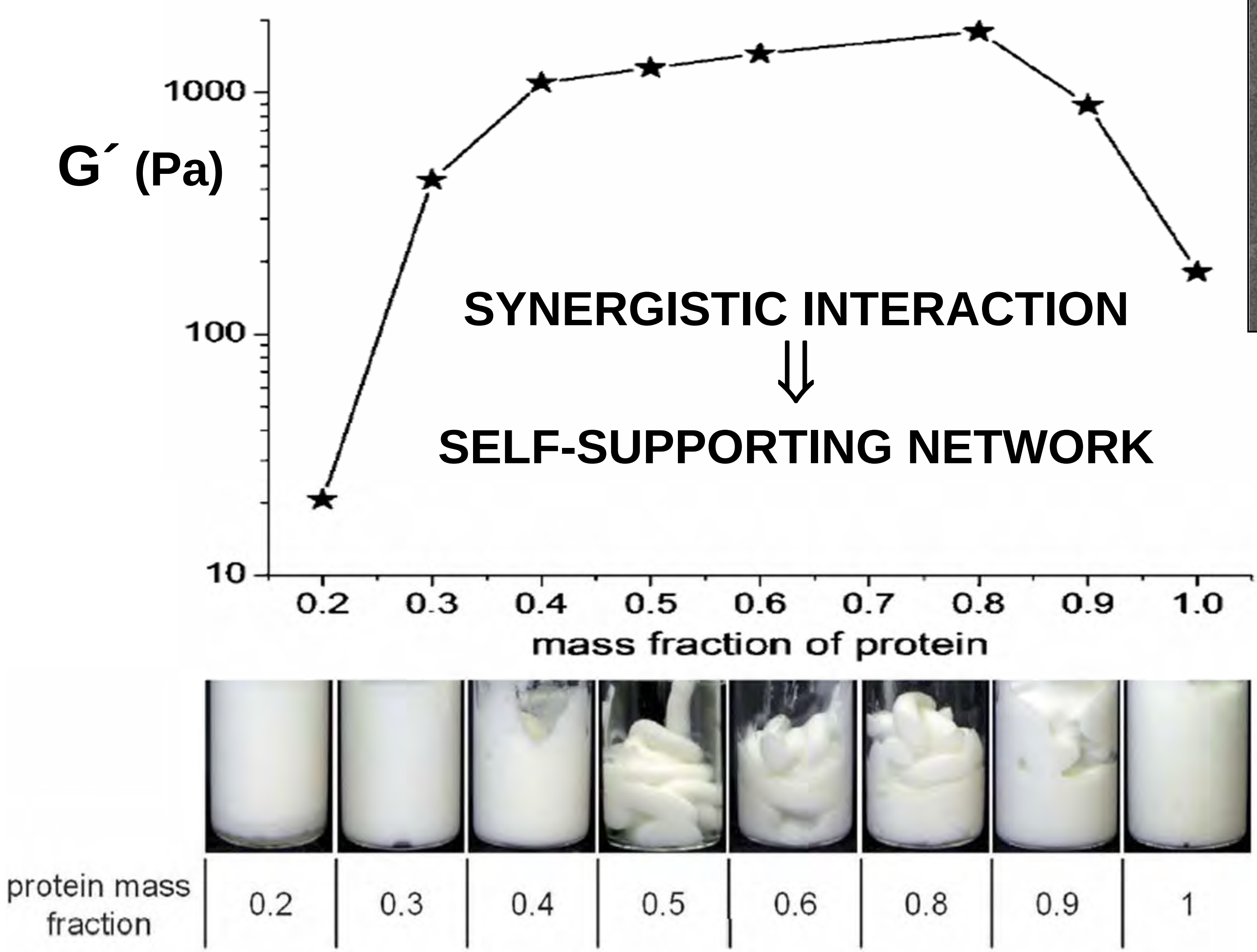
0.5 wt% particles | **0.5 wt% protein** | **0.5 wt% particles + 0.5 wt% protein**

Reger et al., 2011

Stabilization by Mixture of Particles and Protein

Storage modulus (1 Hz)

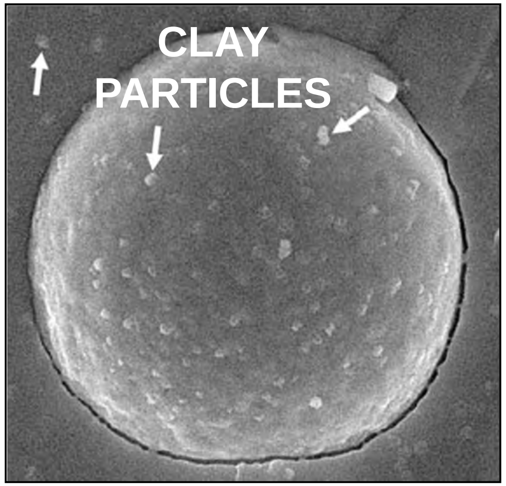
G´ (Pa)

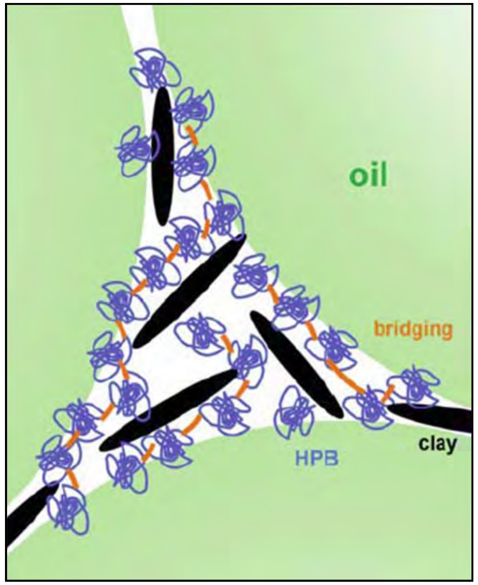


SYNERGISTIC INTERACTION

⇓

SELF-SUPPORTING NETWORK





Reger et al., 2011

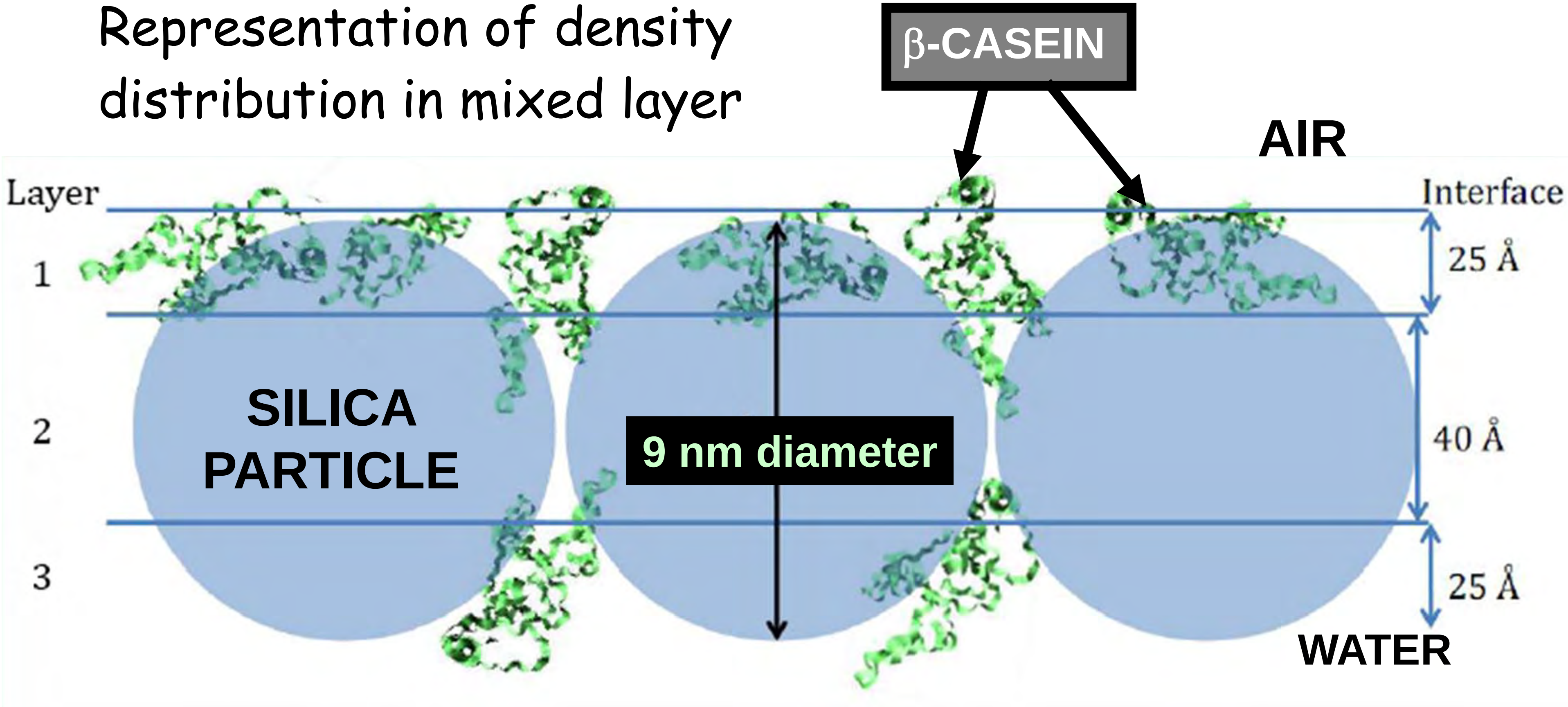
Structure of mixed particle + protein layer?

SYSTEM: β-casein + silica particles (pH = 7) at air–water interface

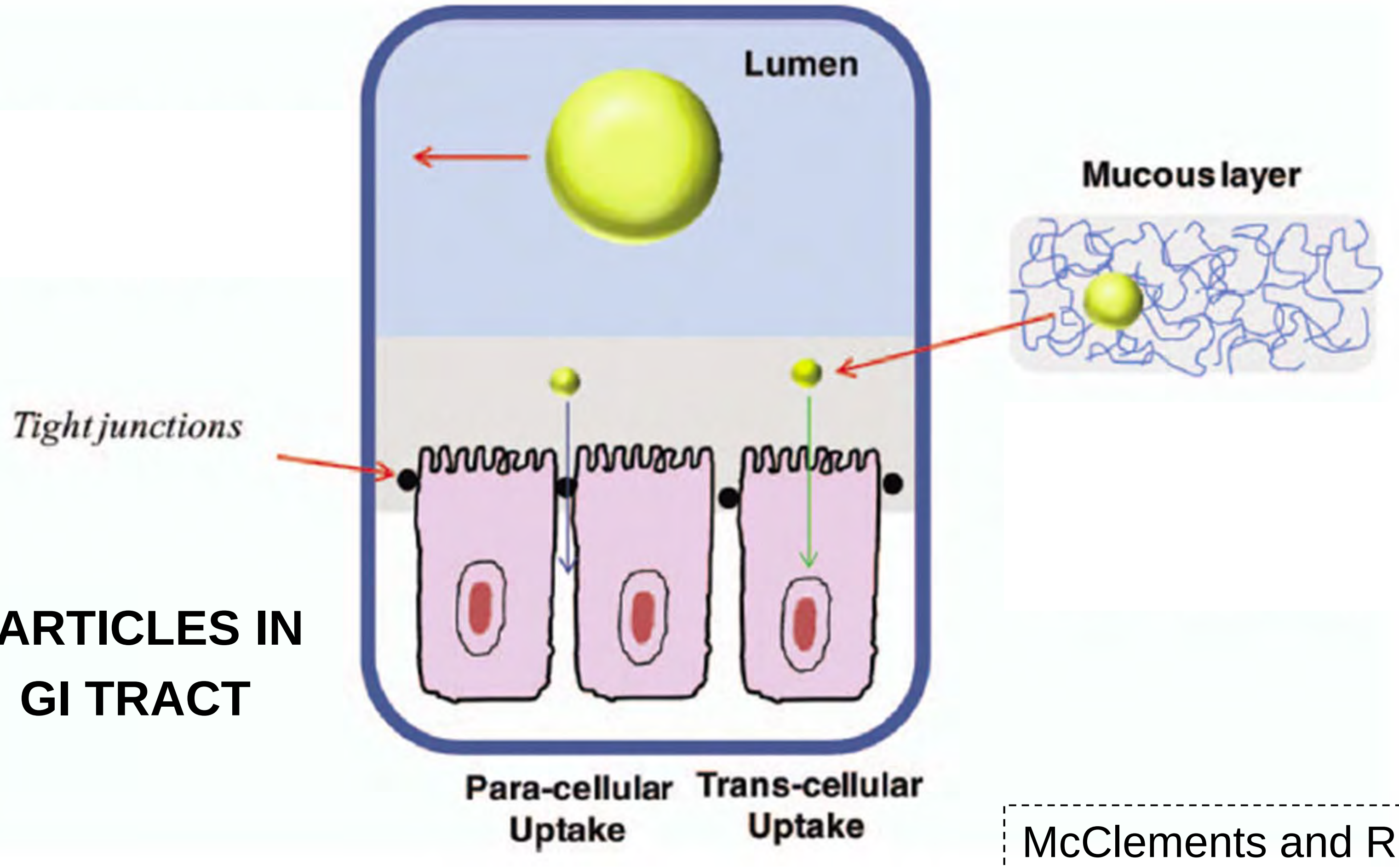
TECHNIQUE: X-ray and neutron reflectivity (with isotropic contrast variation between protein and nanoparticles)

Ang et al., 2010

Representation of density distribution in mixed layer



Safety Issue: What happens to nanoparticles and microparticles in the human body?



PARTICLES IN GI TRACT

McClements and Rao, 2011

Summary

The behaviour of emulsions stabilized by solid particles are substantially different from those of protein-stabilized emulsions.

Emulsions prepared with adsorbed layers of nanoparticles or microparticles can possess outstanding coalescence stability.

In water-in-oil emulsions containing fat crystals, the Pickering mechanism is more effective than fat crystal network stabilization.

Pickering stabilization of food-grade oil-in-water emulsions can be achieved with modified starch particles, chitin nanocrystals, *etc*.

There exist opportunities in the food sector for exploiting the special properties of particle-stabilized emulsions for texture modification, nutrient encapsulation and product quality enhancement.

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