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SCI Conference
“Science & Technology of Food Emulsions”
2012-06-22

Processing of double emulsions

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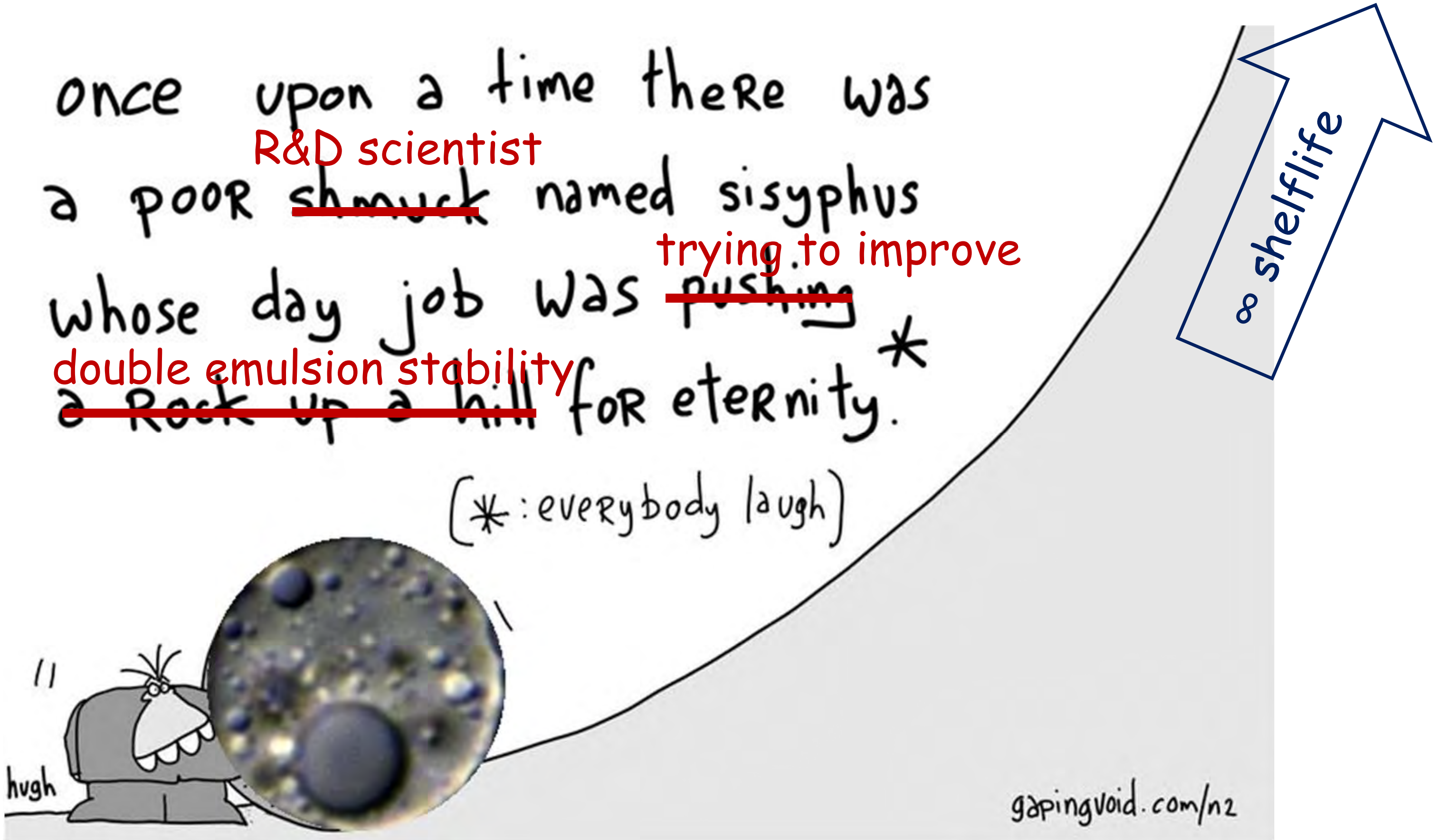
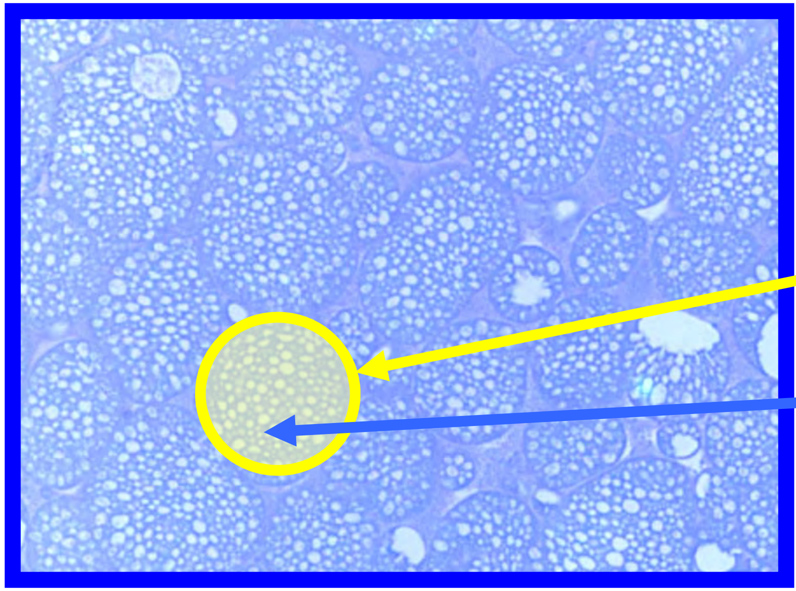
... Sisyphus‘ real pain ...



« … double emulsions are compartmentalised liquid dispersions, in which the droplets of the dispersed phase contain smaller droplets of similar (but not necessarily identical) composition as the continuous phase … »

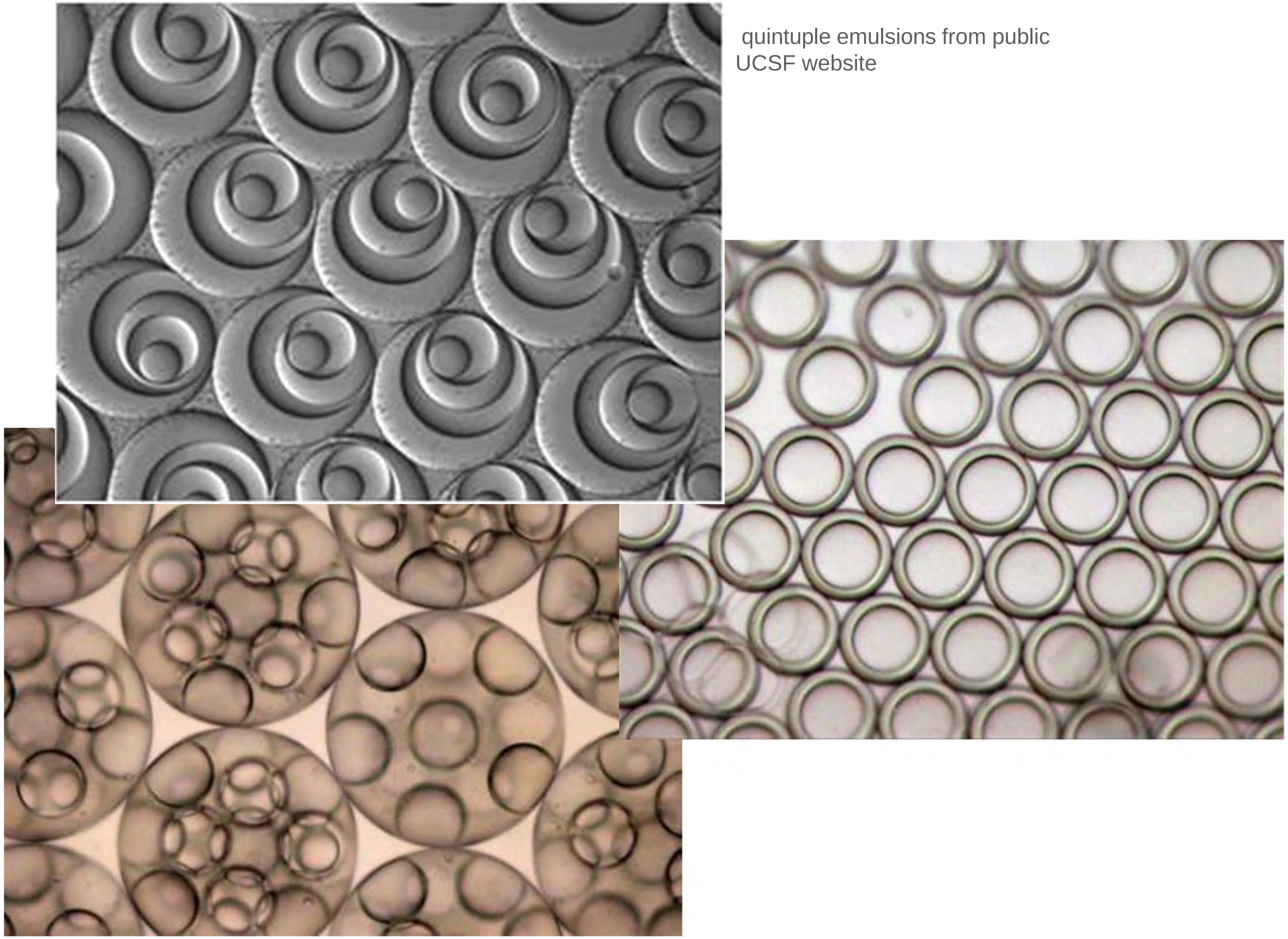


Continuous phase (water)
(=outer emulsion)

Dispersed phase (oil)
(= inner emulsion)

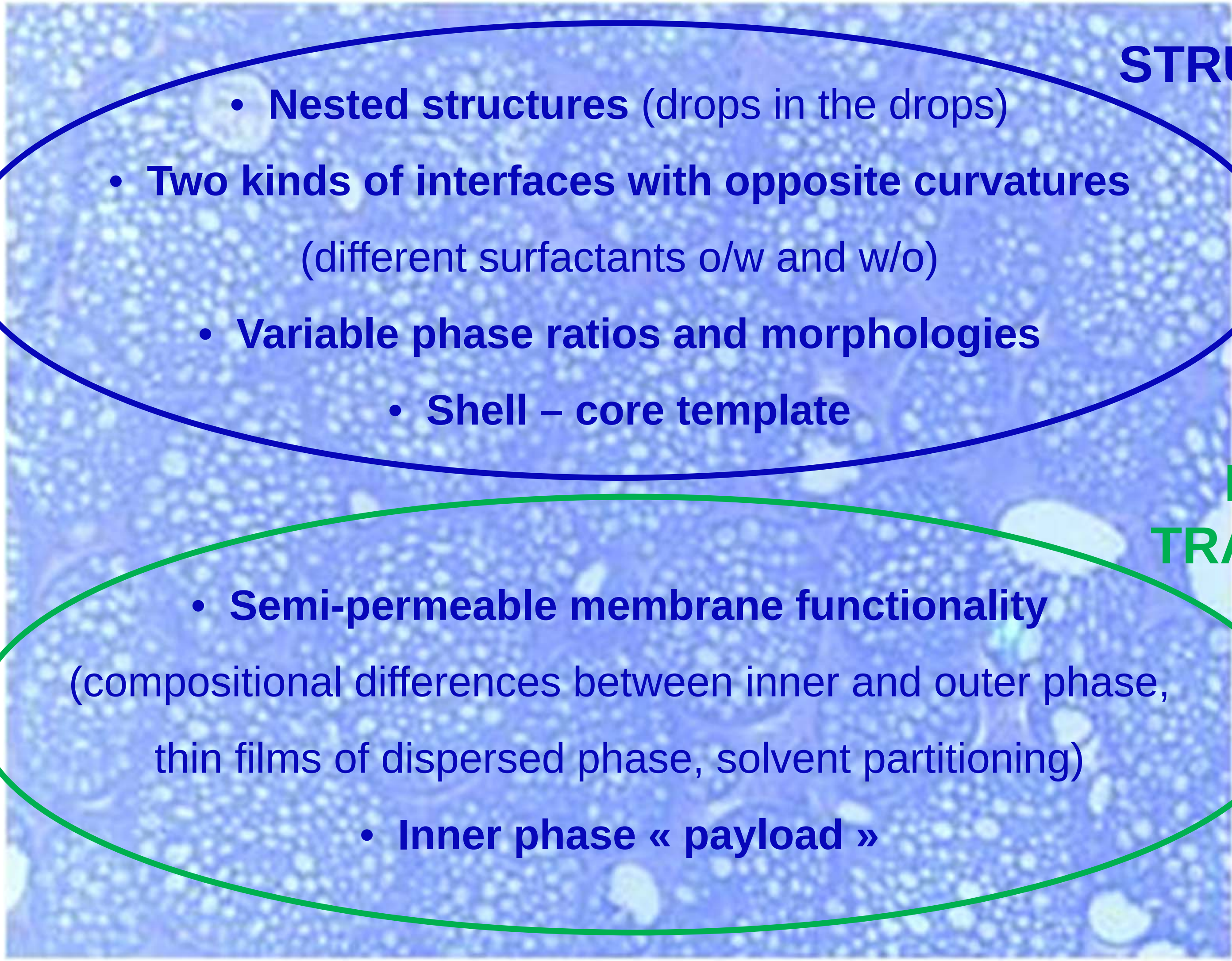
Inner phase (water)

The beauty of multiple emulsions



quintuple emulsions from public UCSF website

Generic features of double emulsions



STRUCTURE

- **Nested structures** (drops in the drops)
- **Two kinds of interfaces with opposite curvatures** (different surfactants o/w and w/o)
- **Variable phase ratios and morphologies**
- **Shell – core template**

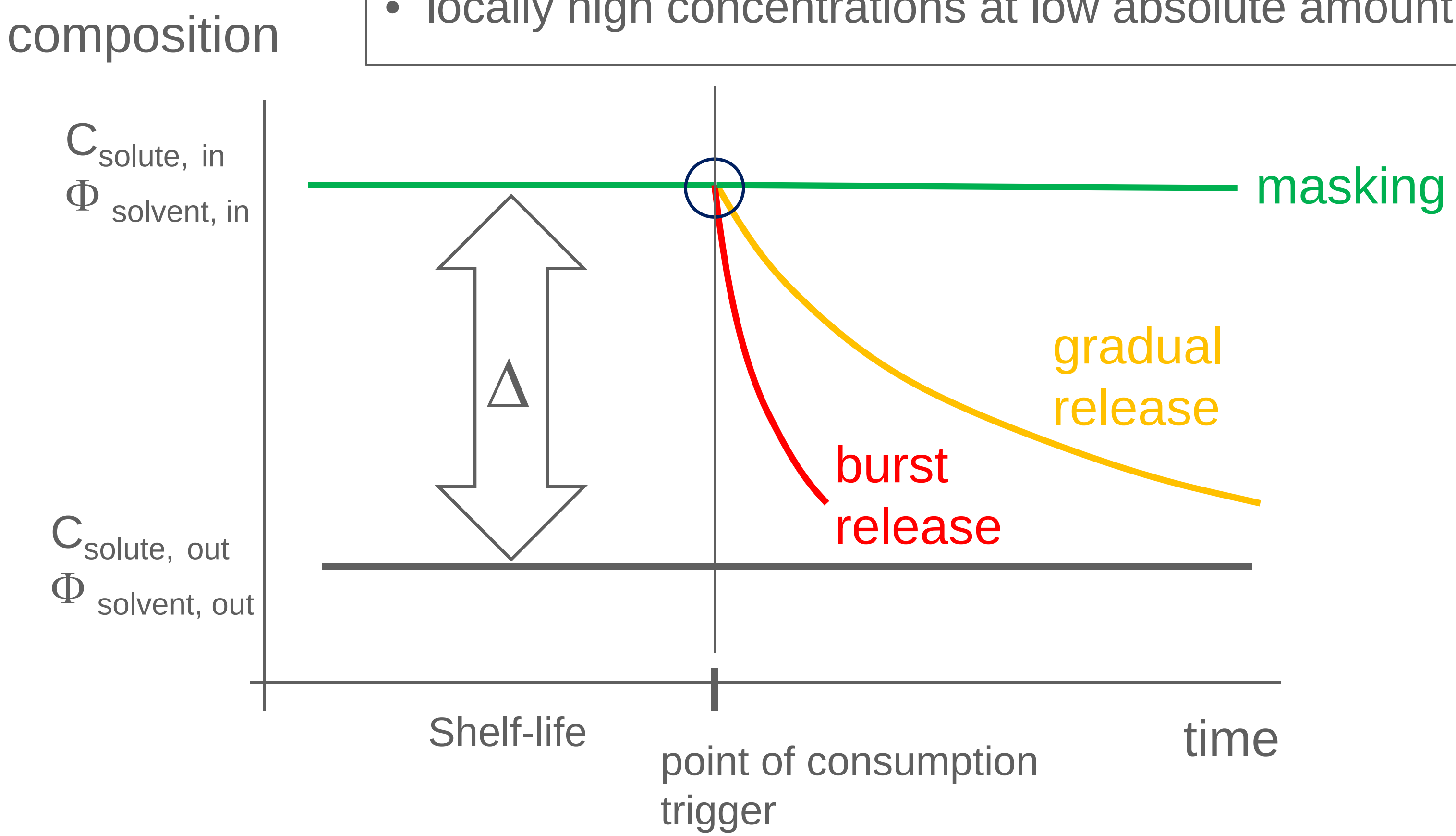
MASS TRANSFER

- **Semi-permeable membrane functionality** (compositional differences between inner and outer phase, thin films of dispersed phase, solvent partitioning)
- **Inner phase « payload »**

Basic types of applications of double emulsions

Compartment structure offers / allows:

- protection (chemical, sensorial) for sensitive material
- locally high concentrations at low absolute amount



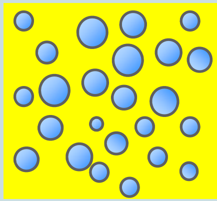
Making double emulsions – the usual 2- step process

Step 1

Oil
+
Emulsifier I

Inner
water phase

High
shear
process



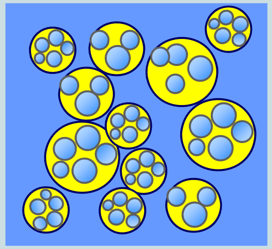
w/o emulsion,
small water drops

Make a primary emulsion with « robust », i.e. small inner water droplets (= high shear)

Step 2

Continuous
water phase
+
Emulsifier II

Low
shear
process



wo / w emulsion,
“large” oil drops

Make final emulsion
with minimum loss
of inner water phase
(= low shear, continuous
«1-shot» processing)

Making double emulsions – other variants

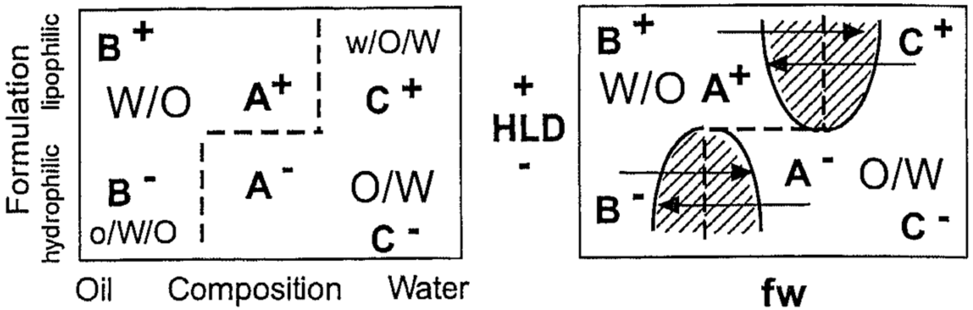


Figure 1. Formulation−composition bidimensional map. Standard (dashed) and dynamic (solid) inversion frontiers.

Zambrano et al., Ind. Chem. Eng. Res., 2003, 42, 50-56

- **(Transient) structure occuring during phase inversion**

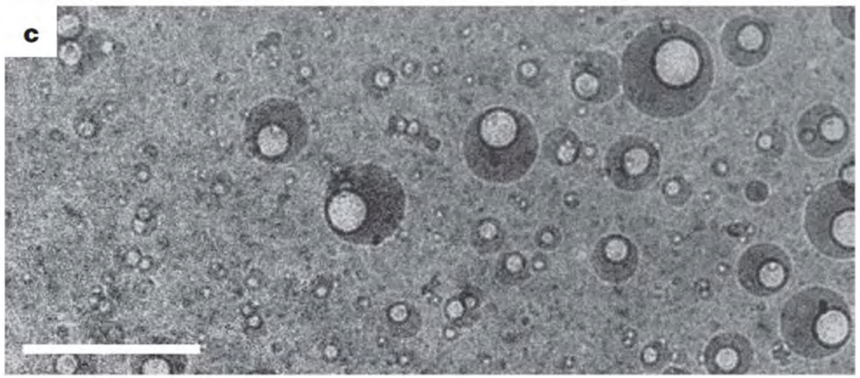


Figure 2 | Cryogenic transmission electron microscopy of copolypeptide-stabilized emulsions prepared using a microfluidic homogenizer. Vitrified

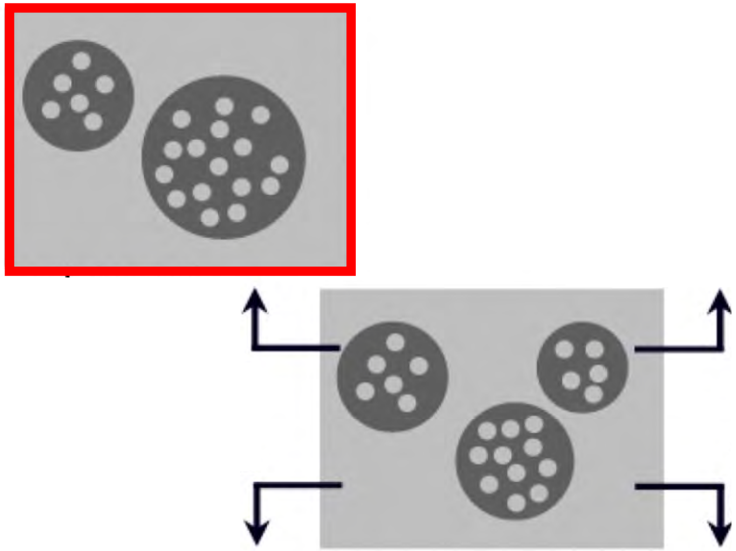
Hanson et al., Nature, vol.455, 2008 (Letters, p.85 ff.)

- **Lucky case of 1-step formation with suitable diblock surfactant**

Pathways of structural changes in double emulsions

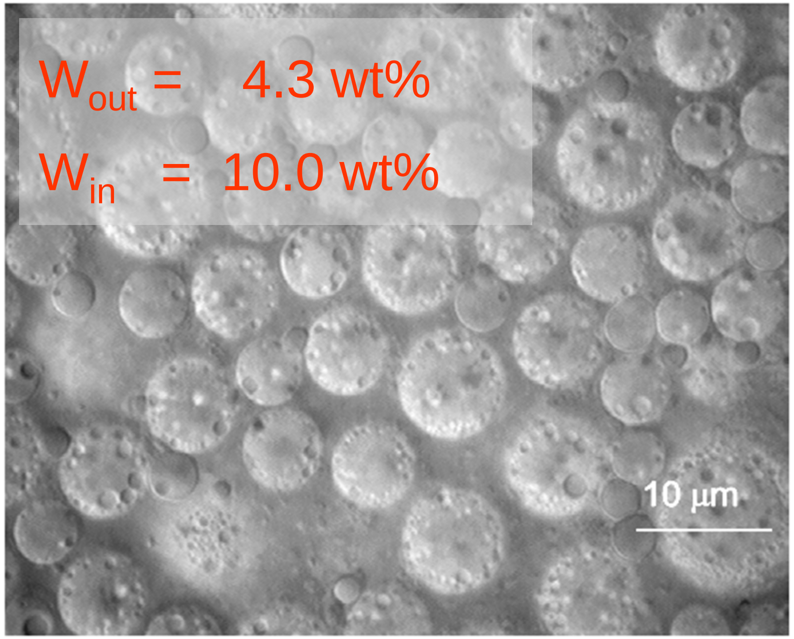
Coalescence of dispersed phase

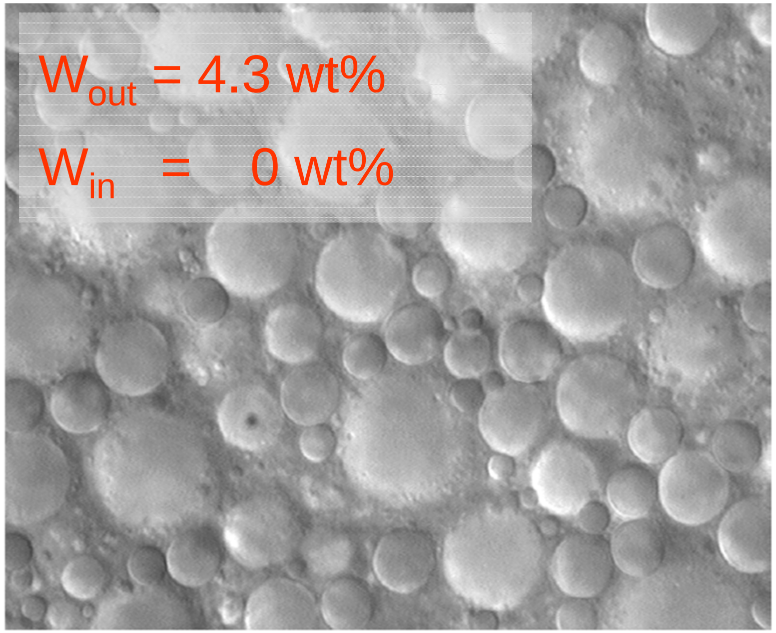
Viscosity loss, oil separation



Survival condition for DE

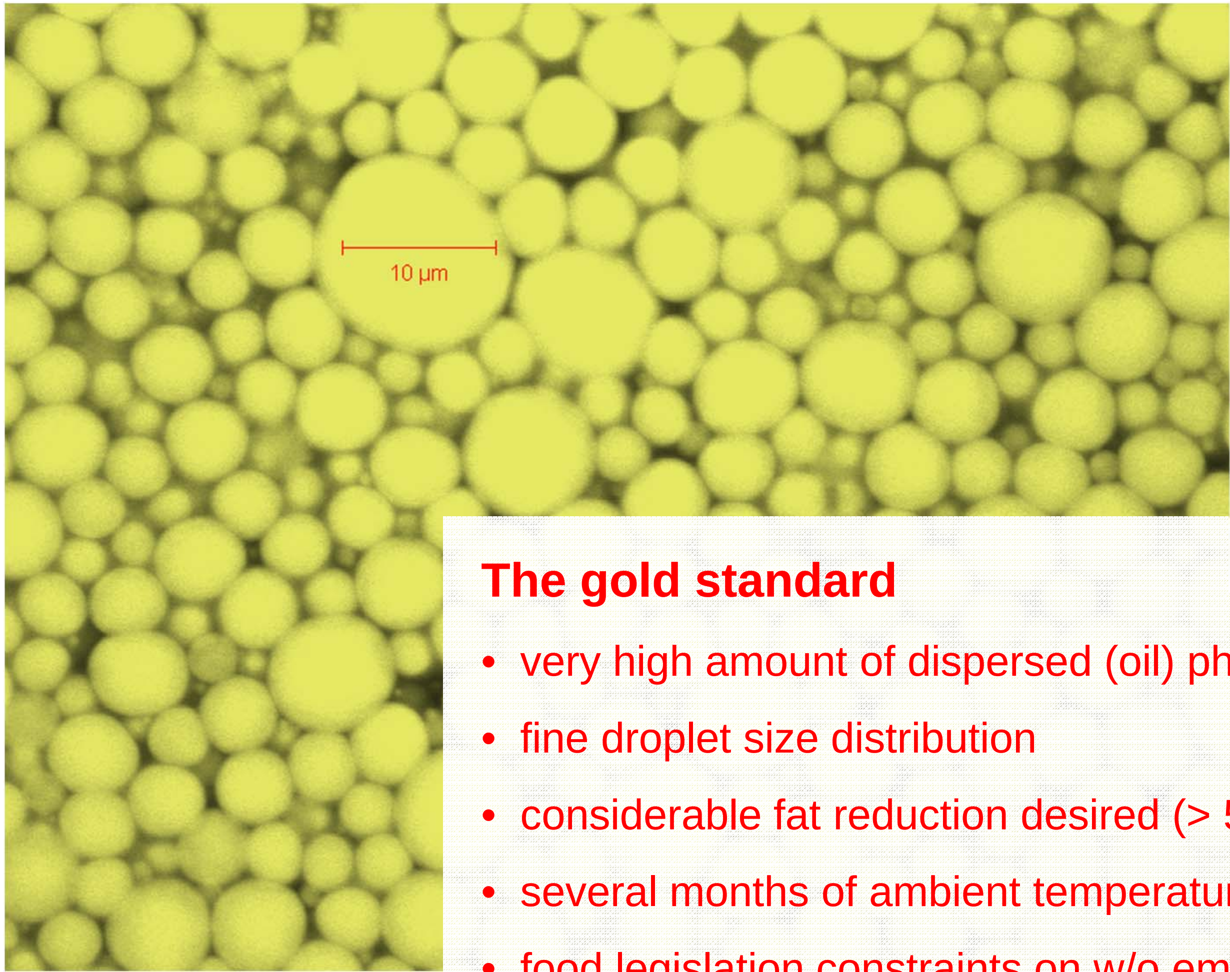
- Membrane system in dynamic equilibrium (continuous diffusion)
- Inner droplets are intrinsically unstable (Laplace pressure)
- DE « lives » from an osmotic pressure gradient that outweighs the Laplace pressure difference





DE samples made with opposite salt concentration gradients, 1 week @4 ° C

Double emulsions – our challenge



The gold standard

- very high amount of dispersed (oil) phase
- fine droplet size distribution
- considerable fat reduction desired (> 50%)
- several months of ambient temperature shelf-life
- food legislation constraints on w/o emulsifier

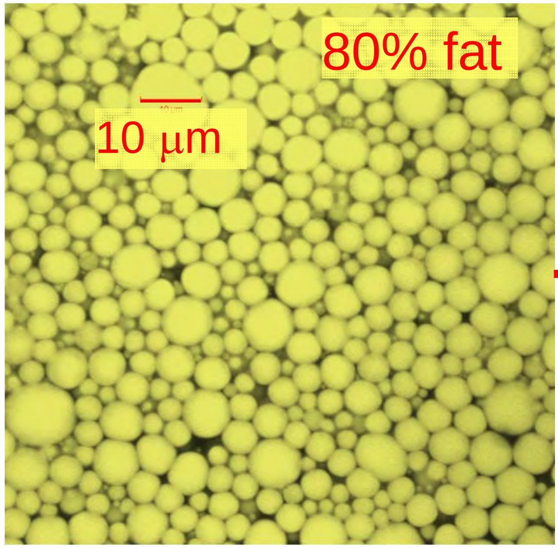
Putting the sensorial hypothesis to the test

« W/o/w emulsion technology offers a sensory perception closer to full fat than the classical thickener approach»

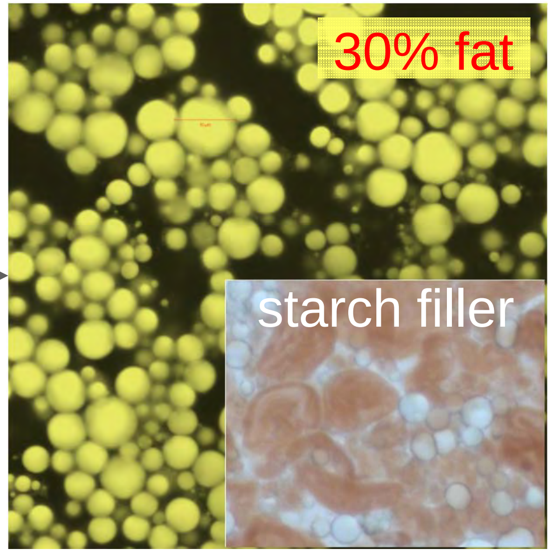
- Keep high (apparent) oil phase ratio and specific surface area
- Dispersed phase « stuffing » less readily perceived in the mouth than a continuous phase dilution
- Replacing oil by a liquid, not by a « viscoelastic microsponge » of much larger size
- Maintain oil droplet interaction forces

Less fat – one goal – two ways

The reference

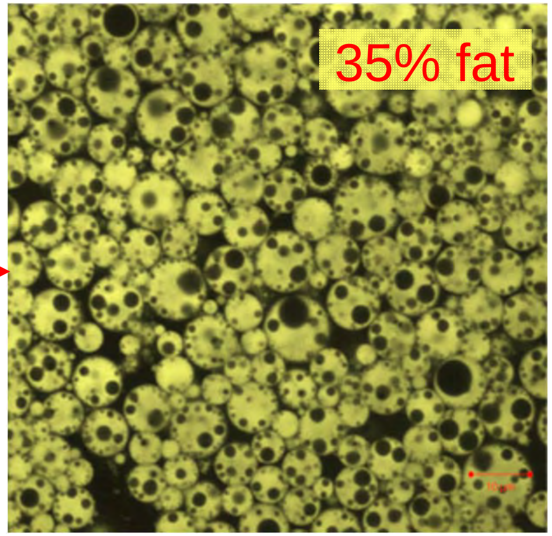


Mayonnaise owes its texture & taste to a space-filling oil phase



Classical low–fat mayo

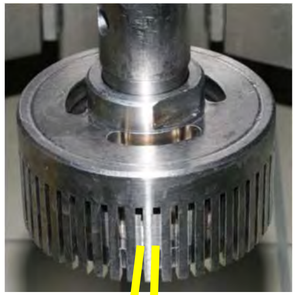
- Dilute continuous phase with starch & thickener paste
- Draw-back:
  mouthfeel thickener-controlled, compromise on texture & taste



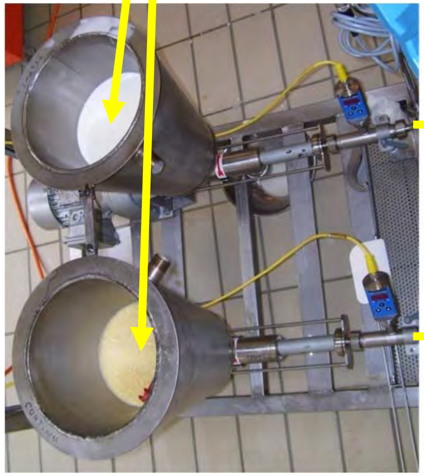
Double emulsion

- «Stuff» oil phase with water
- Benefit:
  Space-filling oil phase is apparently maintained, close to full fat perception

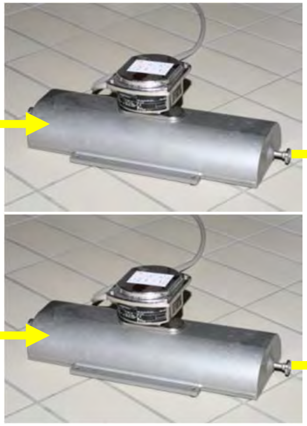
2-step process realisation at bench-scale



w/o emulsions & external water phase W_{ext}
- RS-mixer (0.5-3 krpm)
- batch (8-50 kg)
- degassing (optional)



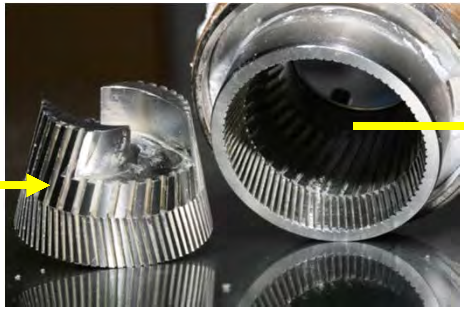
Dosing
- volumetric pumps
- total flow 5 - 20 kg/h
- temperature 15 - 20° C



Mixing ratio wo/W
- 2 mass flow meters
- measures m*, T_{in}, ρ
  (allows foam detection)

"Pre-emulsion"

- static mixer
- pinstirrer



"1-shot" emulsification
- IKA MagicLab MKU colloid mill
- rot. speed = 6.6 (3.5 -12) krpm
- gap = 0.16 mm, volume = 0.2 cm^3
- backpressure = 0.5 bar (for stable dosing, pneumatic valve)

Packaging & storage
- single-use cups
  (serrated, PP, 125 ml)

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Same final line settings, same recipe,
two very different results depending on flow rate history,
effect more pronounced for low w/o ratios

Initial yield stress = 140 Pa

Initial yield stress = 50 Pa

6 months storage 18° C, initially both homogeneous

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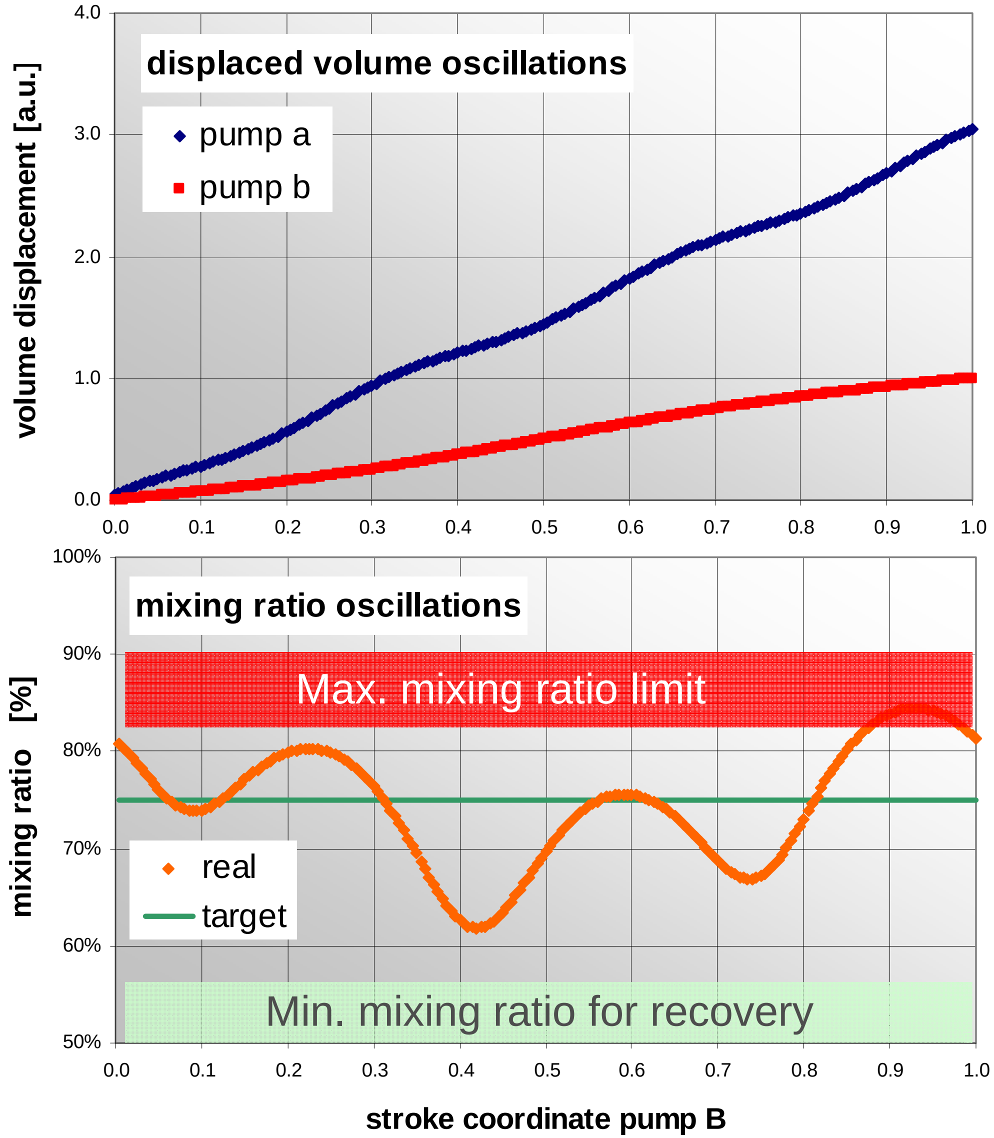
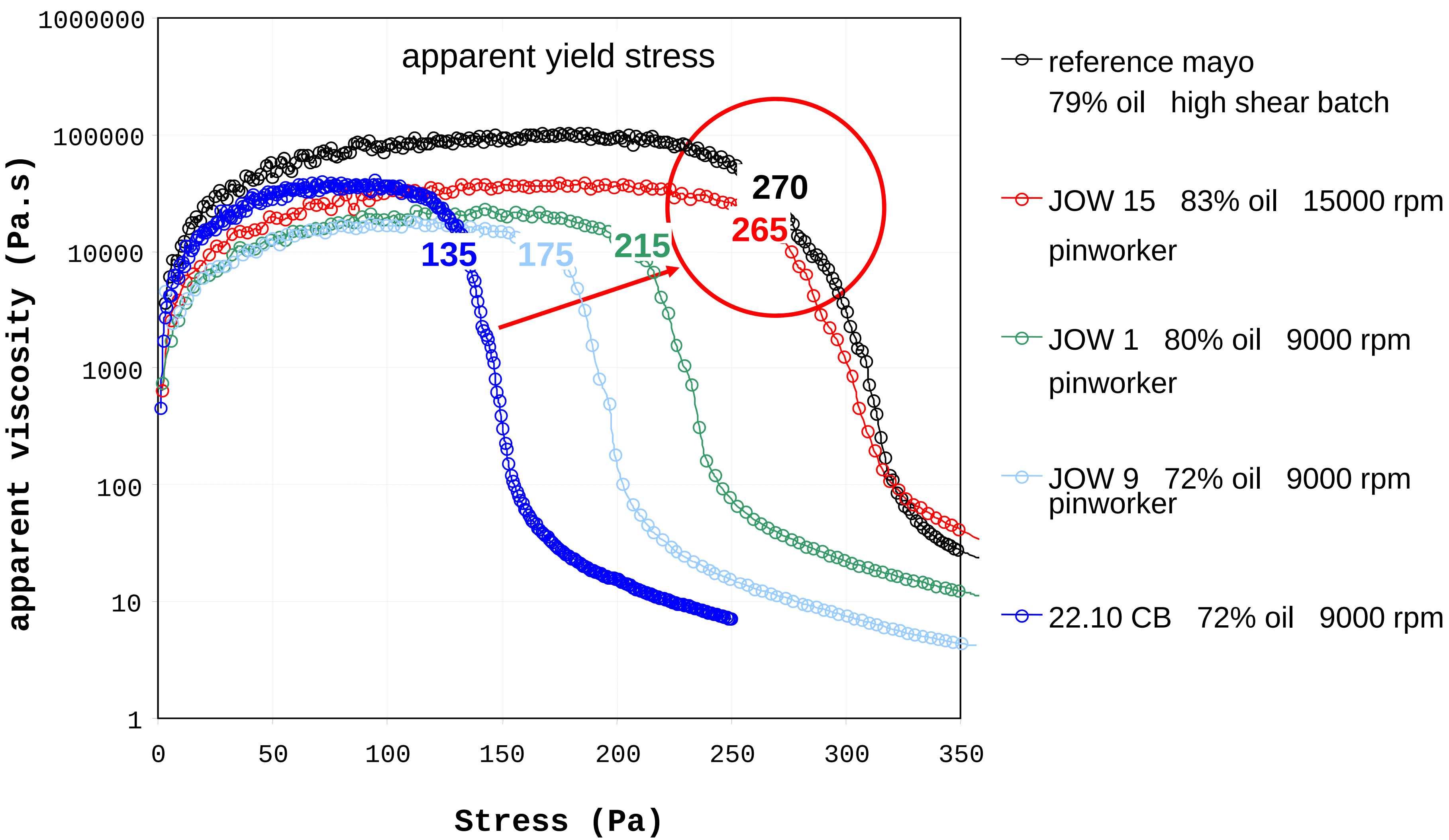
... if you want to make it too simple ...

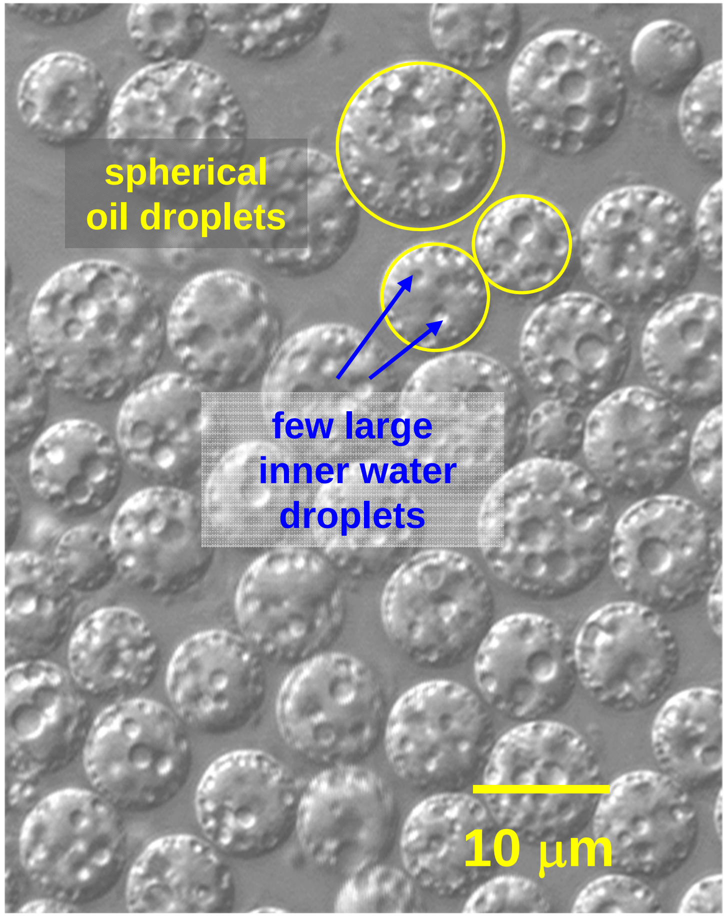


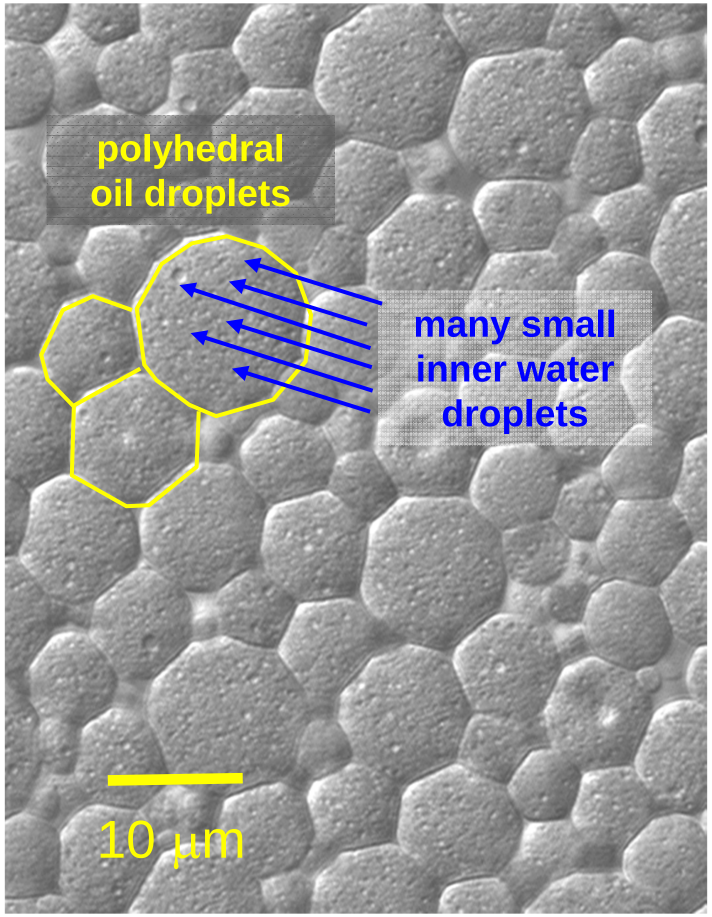
- Emulsion premix must not exceed a critical mixing ratio at the volume scale of the dispersing zone
- Dosing fluctuations or coarse pre-emulsions can generate critical feed volume units
- Depending on the hysteresis characteristics, the system does recover or not
- “In-process leakage” of DE dilutes the continuous phase and allows higher mixing ratios than for o/w

... catch up to the o/w reference with appropriate premixing ...



Double emulsions – some examples of experimentally obtained drop size distributions





Overworking DE at high rpm

Three levels of analysis

Level 0 — Basic sample assessment

Use standard methods for judging sample quality and its evolution over time

Level -1 — Quantify water population of real samples

Develop suitable methods for following the water exchange process between inner and outer phase

Level -2 — Study key processes (water exchange, coalescence, emulsifier behaviour) in laboratory experiments

Mimic water transport in multi-capillary tensiometric device,
study coalescence in drop micromanipulator,
classify interfacial properties of suitable wo emulsifiers,

Our method selection

« Pragmatic » analytics

- Sedimentation / serum separation (visual)
- Rheological behaviour (vane)
- Droplet sizing by light scattering / optical microscopy
- Confocal microscopy (fat staining)
- Conductivity

« Explorative » analytics

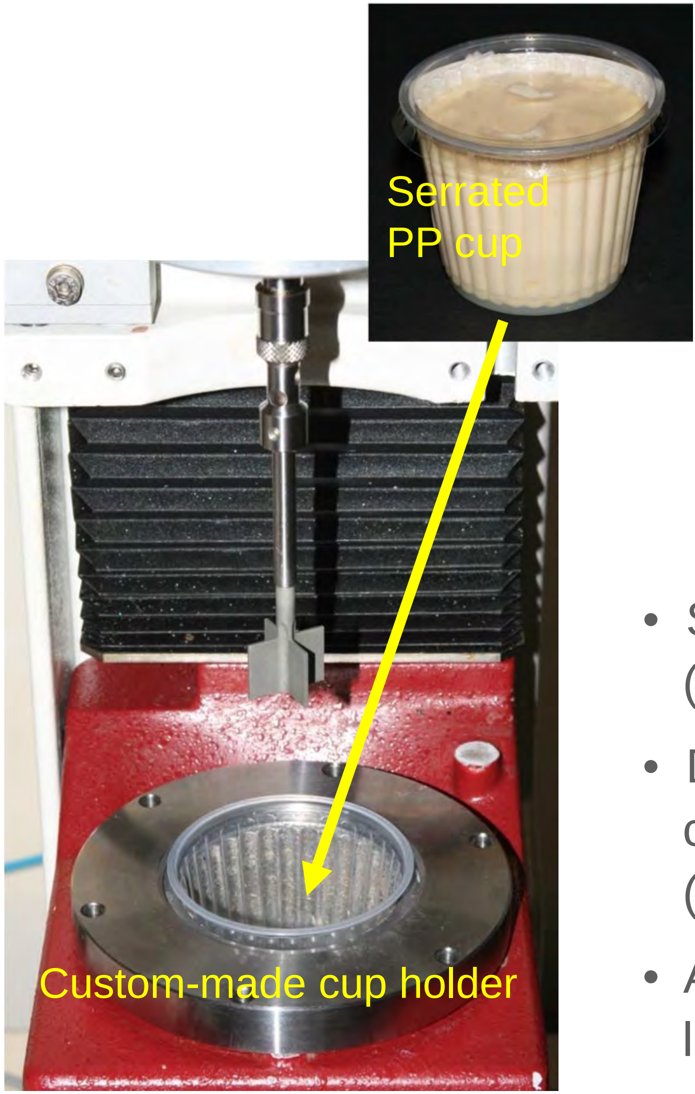
- Quantification of internal and external water populations
  NMR self-diffusion
- Combined electrochemical method (Na^{+}-specific electrode & conductivity)

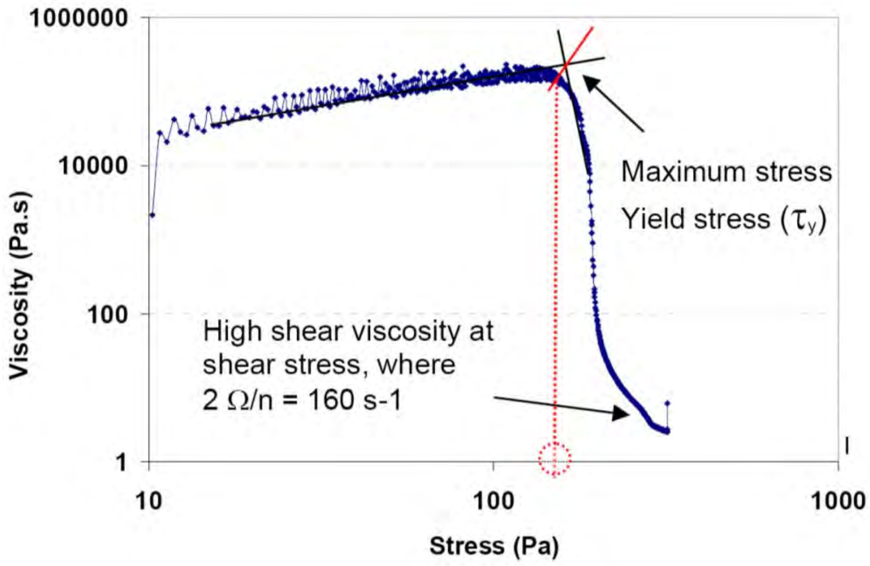
Visual appearance

Qualitative visual observation of :

- Serum formation (amount, time)
- Gel character of creamed fat phase
- Presence of free oil

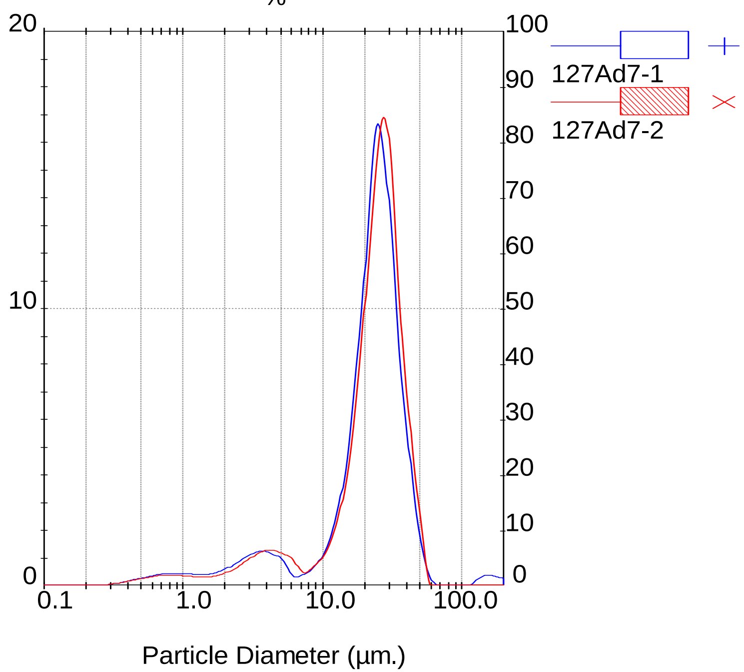
Vane rheology

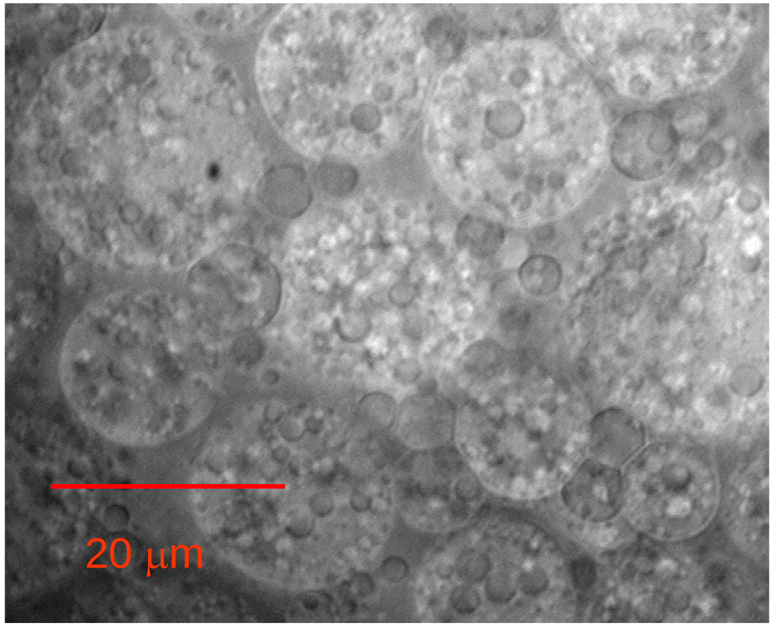




- Stress-controlled, serrated cups (avoid wall slip)
- Determination of «yield stress», power law coefficient and high shear rate viscosity (composite Ellis model)
- Advantage of single-use cups + vane = low mechanical disturbance of sample

Static light scattering





Conc. = 0.0185 %Vol	Density = 1.000 g/cm^3	S.S.A.= 0.6556 m^2/g
Distribution: Volume	D[4, 3] = 24.09 um	D[3, 2] = 9.15 um
D(v, 0.1) = 5.14 um	D(v, 0.5) = 24.80 um	D(v, 0.9) = 38.29 um
Span = 1.337E+00	Uniformity = 3.610E-01	

- Droplet sizing with Mastersizer (issues: destabilisation of primary emulsion, deflocculation, swelling of double emulsions)
- Qualitative cross-check with optical microscopy (issues: opacity, sample compression & capillary stresses, coalescence)

Confocal microscopy

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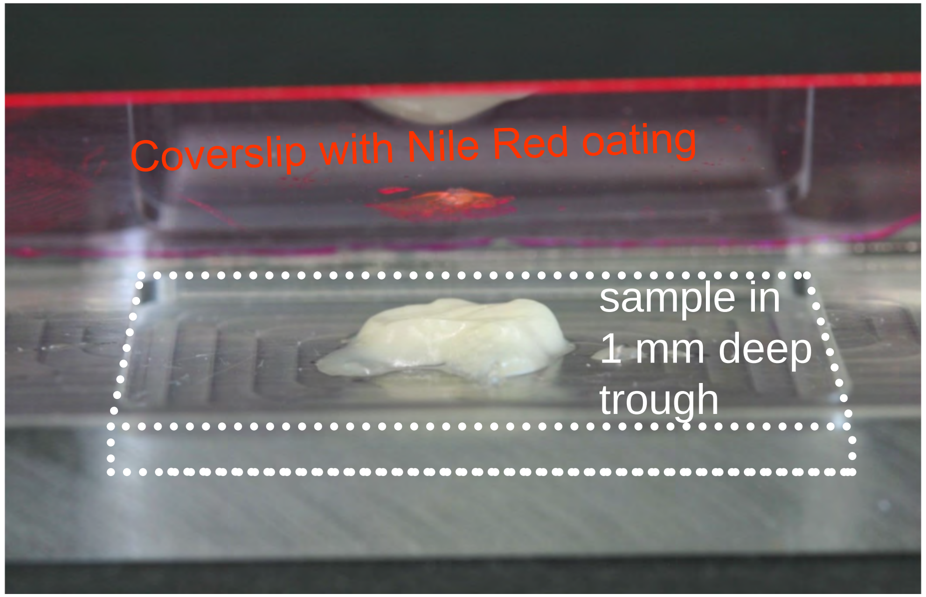

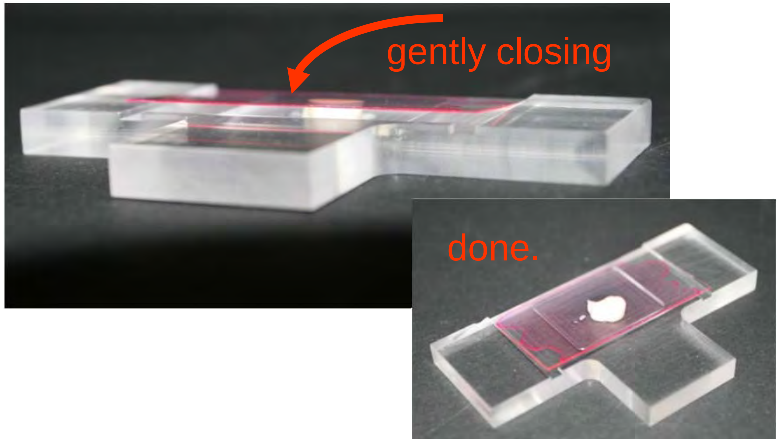

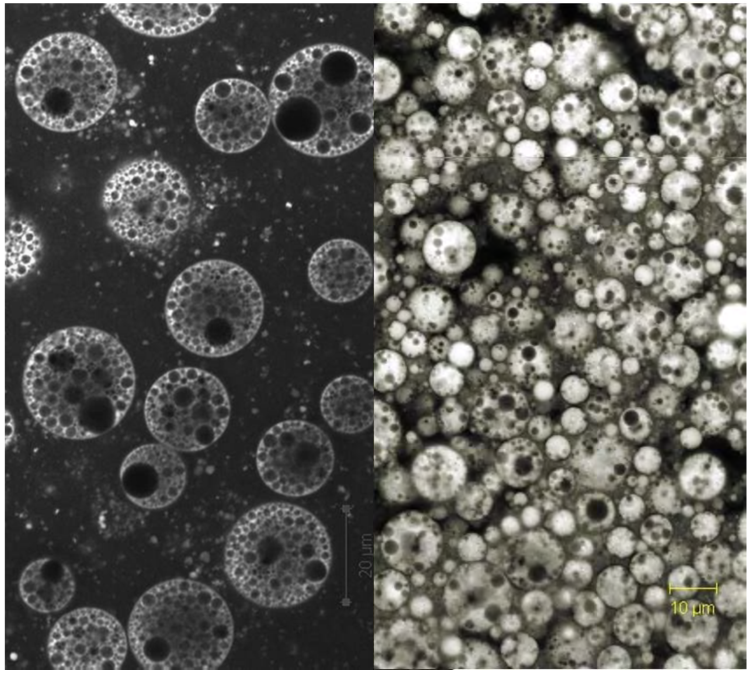

- Diffusive Nile Red staining of fat phase
- Reduced compression and capillary stresses acting on sample
- No dilution = visualization of space filling
- Qualitative check of droplet sizes and filling with inner phase

Intrinsic problem of conductivity measurements for determination of DE water populations

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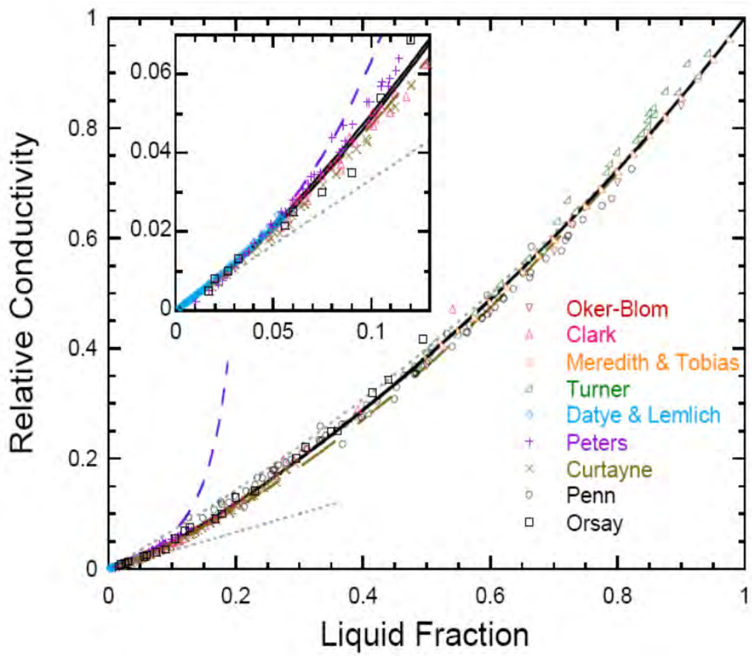
Simple emulsions

$\sigma_{abs} = \sigma_{ext} * f(\Phi)$



Double emulsions - complications

- Water diffusion:
  counteracting, partially outweighing effects on σ(ext) and f(Φ)
- Inner phase leakage:
  σ(ext) and f(Φ) effects add up ⇨theoretically possible
- Combined diffusion and leakage:
  Variable mixing of inner and external phase, σ(ext) can vary strongly for constant Φ_{ext}

⇨ Φ_{ext} determination is ambiguous , but noticeable conductivity increase indicates inner phase leakage

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Combined electrochemical method for evaluation of water population

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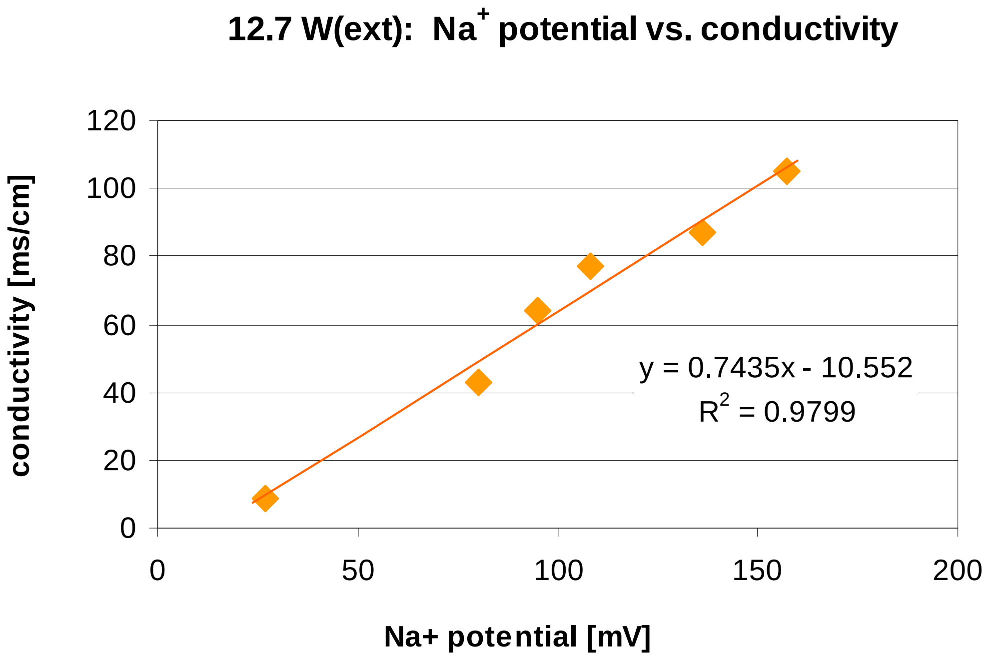

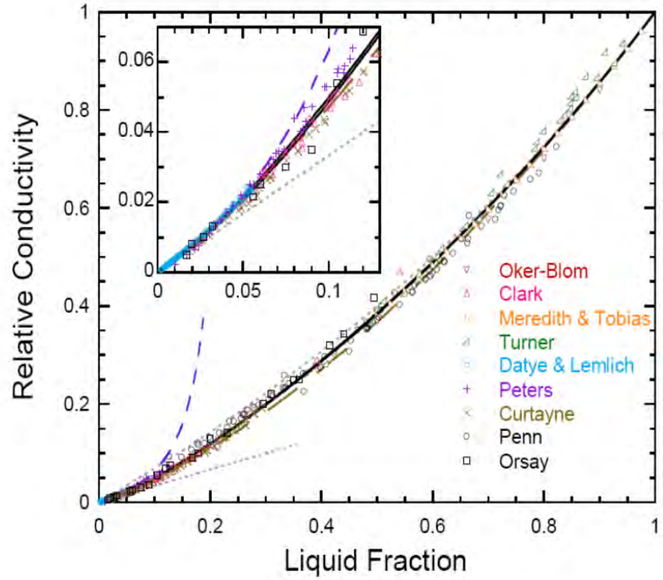

- conductivity of W_{ext} dominated by NaCl
- $c[Na^{+}]$ sufficiently well measured with Na-specific electrode
- clear relationship $\phi(Na^{+})$ - σ_0 (from $\phi=\phi(c[Na^{+}])$ and $\sigma=\sigma(c[Na^{+}])$ curves)

⇨ measurement of water population and salt leakage seems feasible

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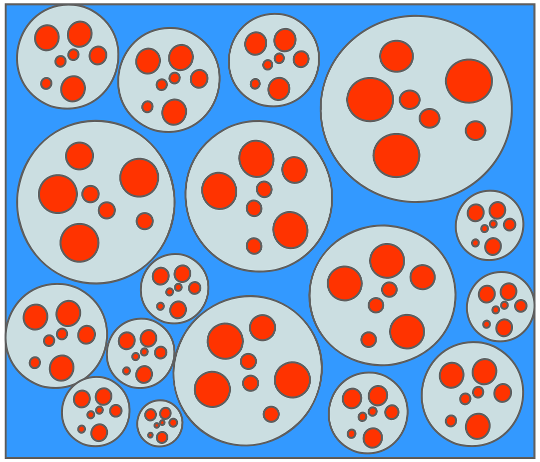
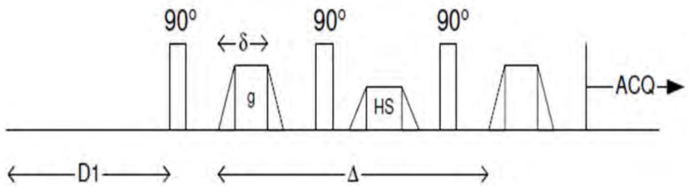
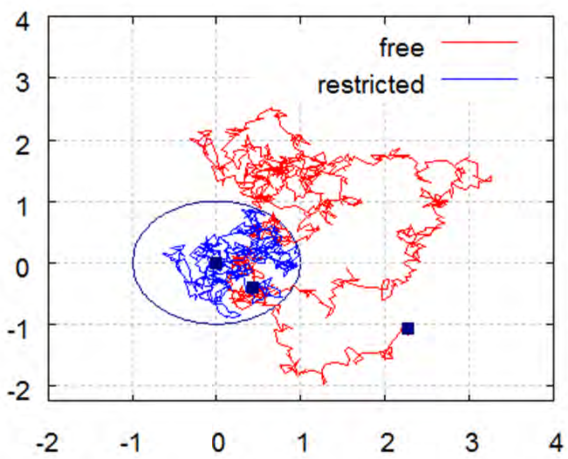
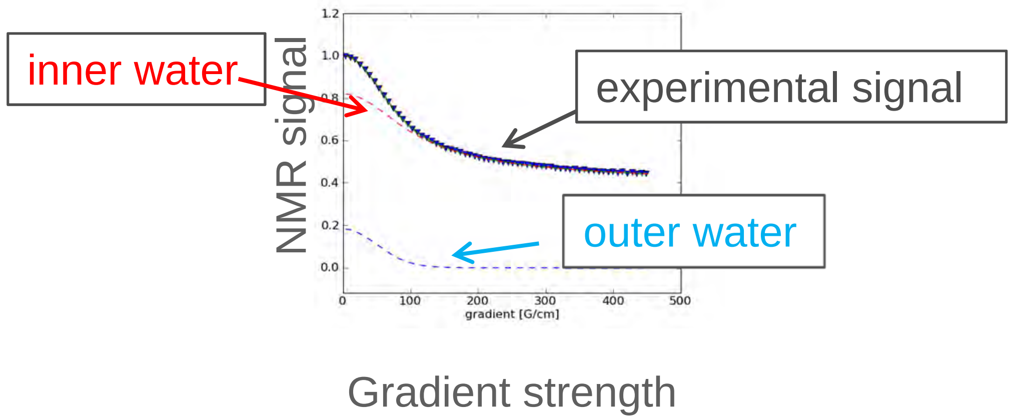


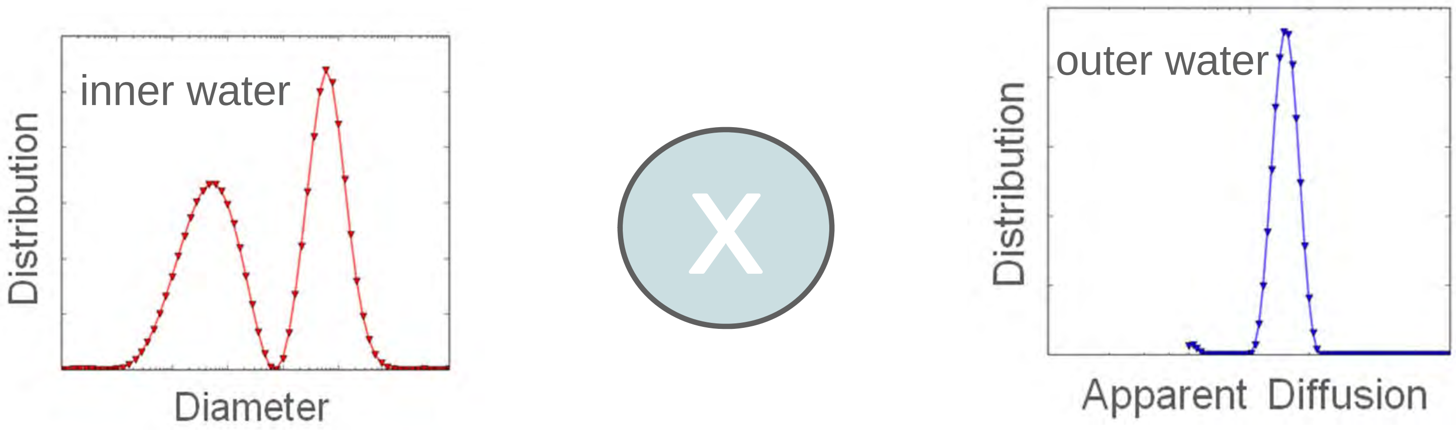


NMR diffusion experiment of water in double emulsion

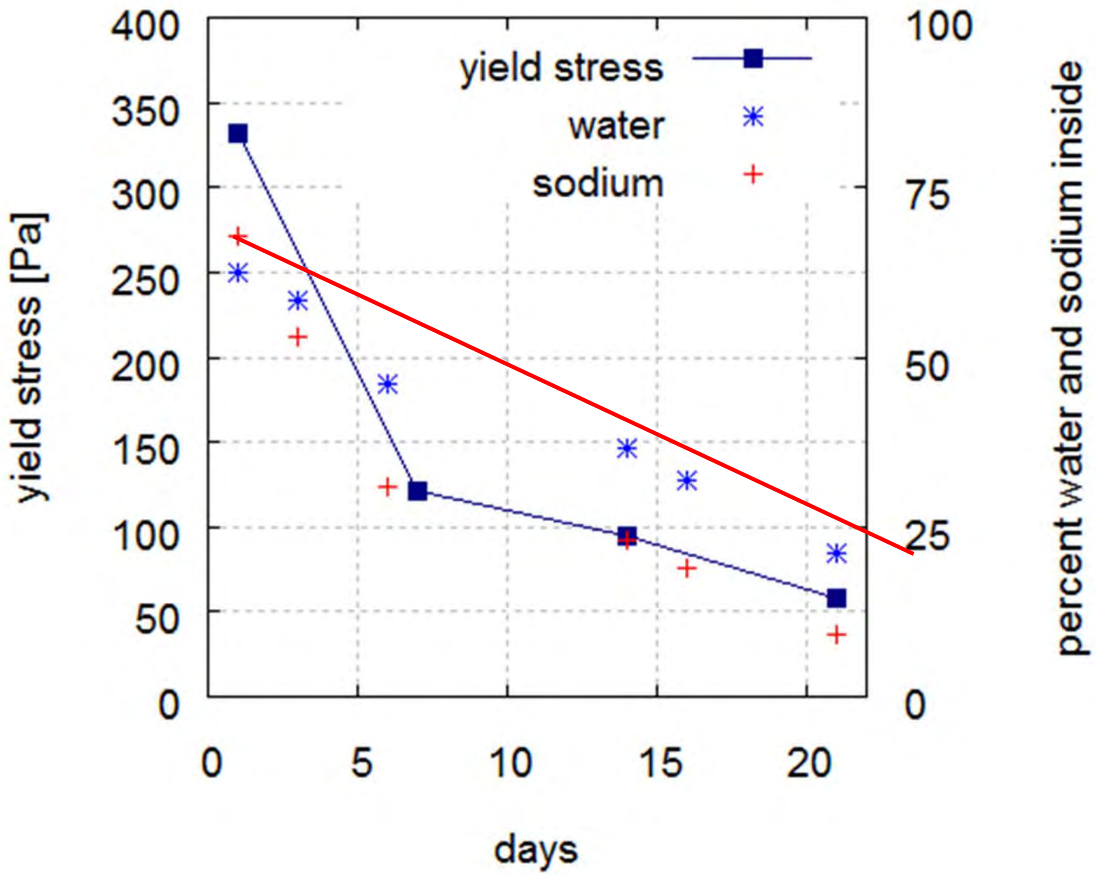




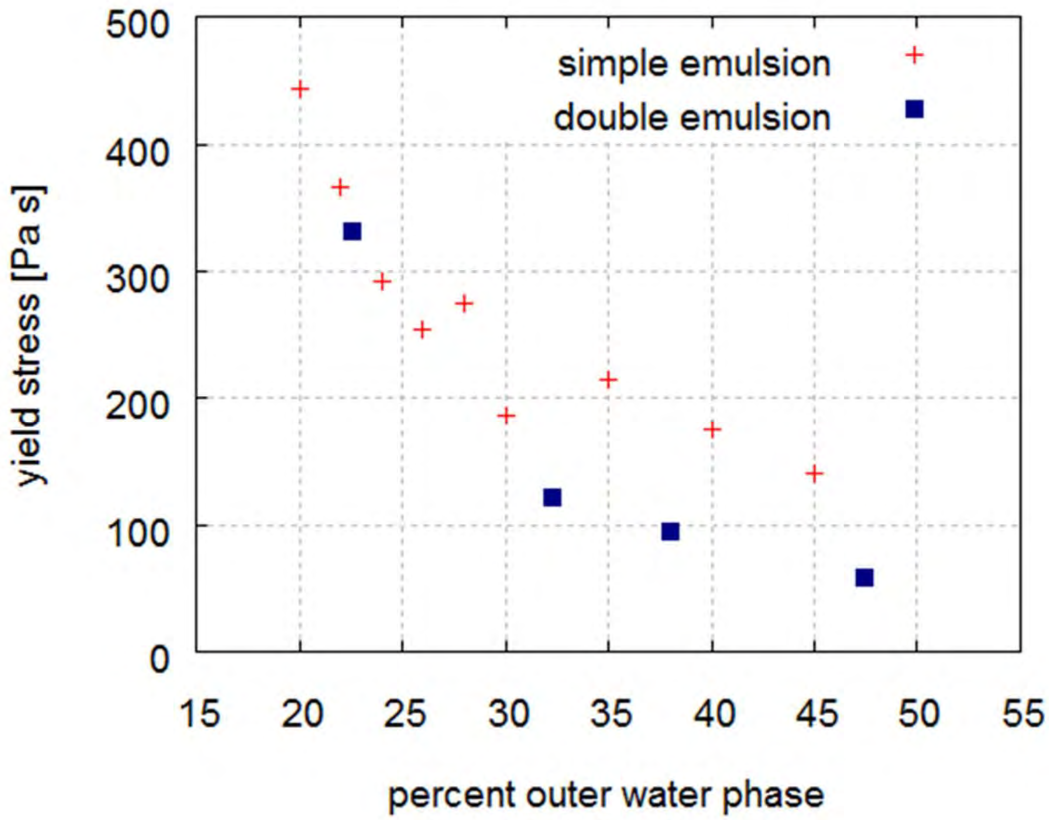
NMR diffusion signal is a function of the unknown inner water droplet distribution and the unknown outer hindered diffusion distribution



Correlation of yield stress and water population evolution



Yield stress comparison of simple and double emulsions, according to NMR water population data



simple emulsion	double emulsion
Wo $= 100 \times w_o / (w_o + oil)$	$= 100 \times w_o / (w_o + w_i + oil)$

Serum separation is diluted simple emulsions is similar to DE behaviour

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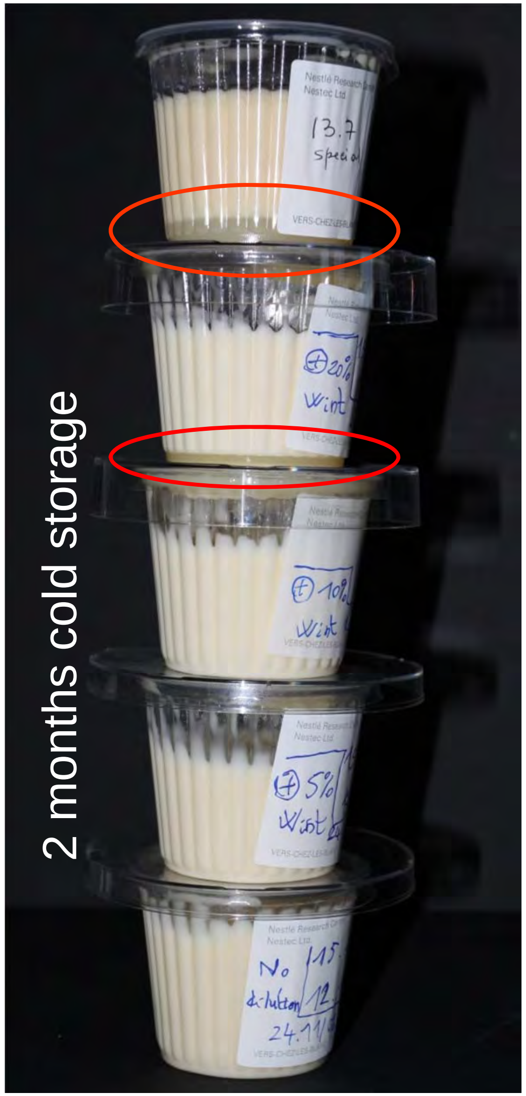


“Jammed” droplet network is lost beyond a critical dilution ⇨ droplet compacting & drainage

≈ 50% oil : 60/40 emulsion diluted with 20% W_{intern}
(= 80/20 diluted with 30% W_{extern} and 20% W_{intern})

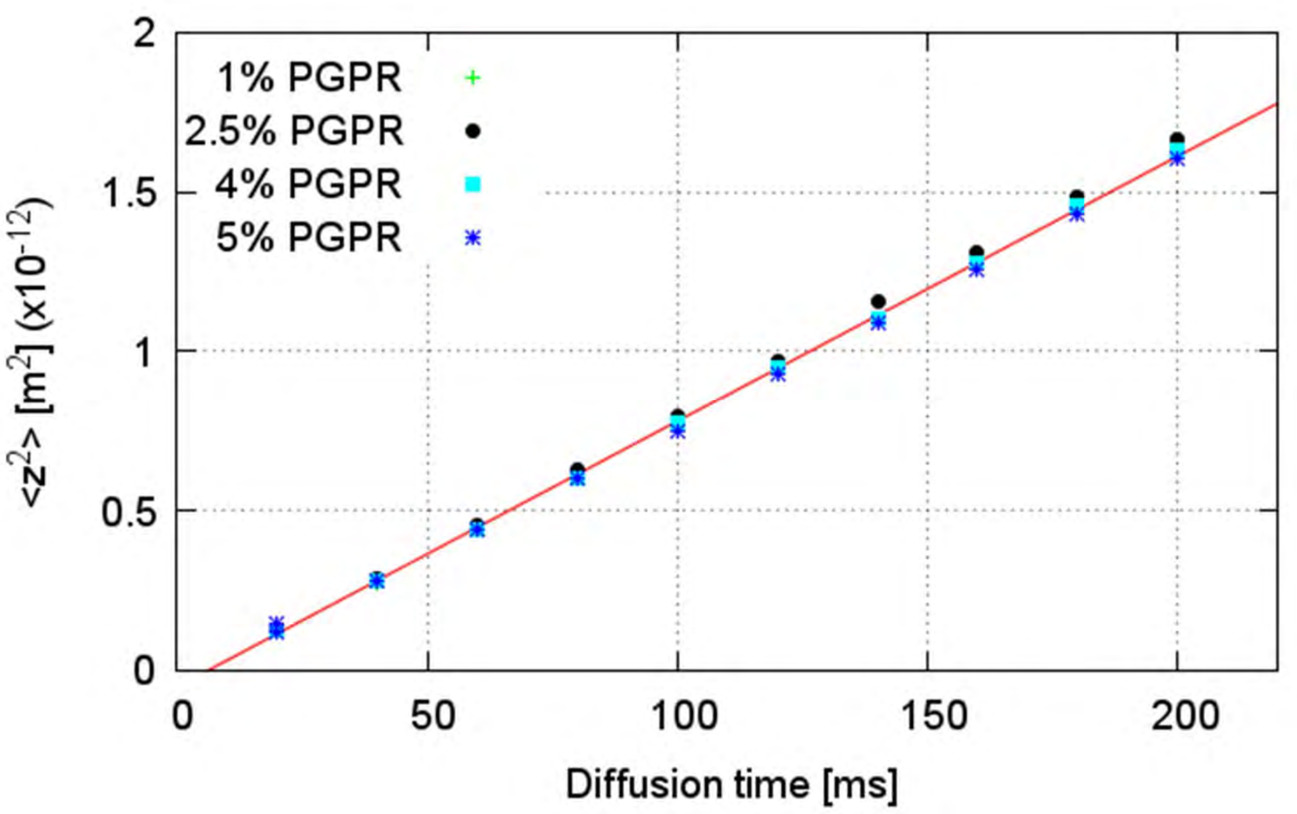
≈ 67% oil : diluted with 20% W_{intern}

≈ 73% oil : diluted with 10% W_{intern}

≈ 76% oil : diluted with 5% W_{intern}

80% oil : NRC full fat mayo, stirred

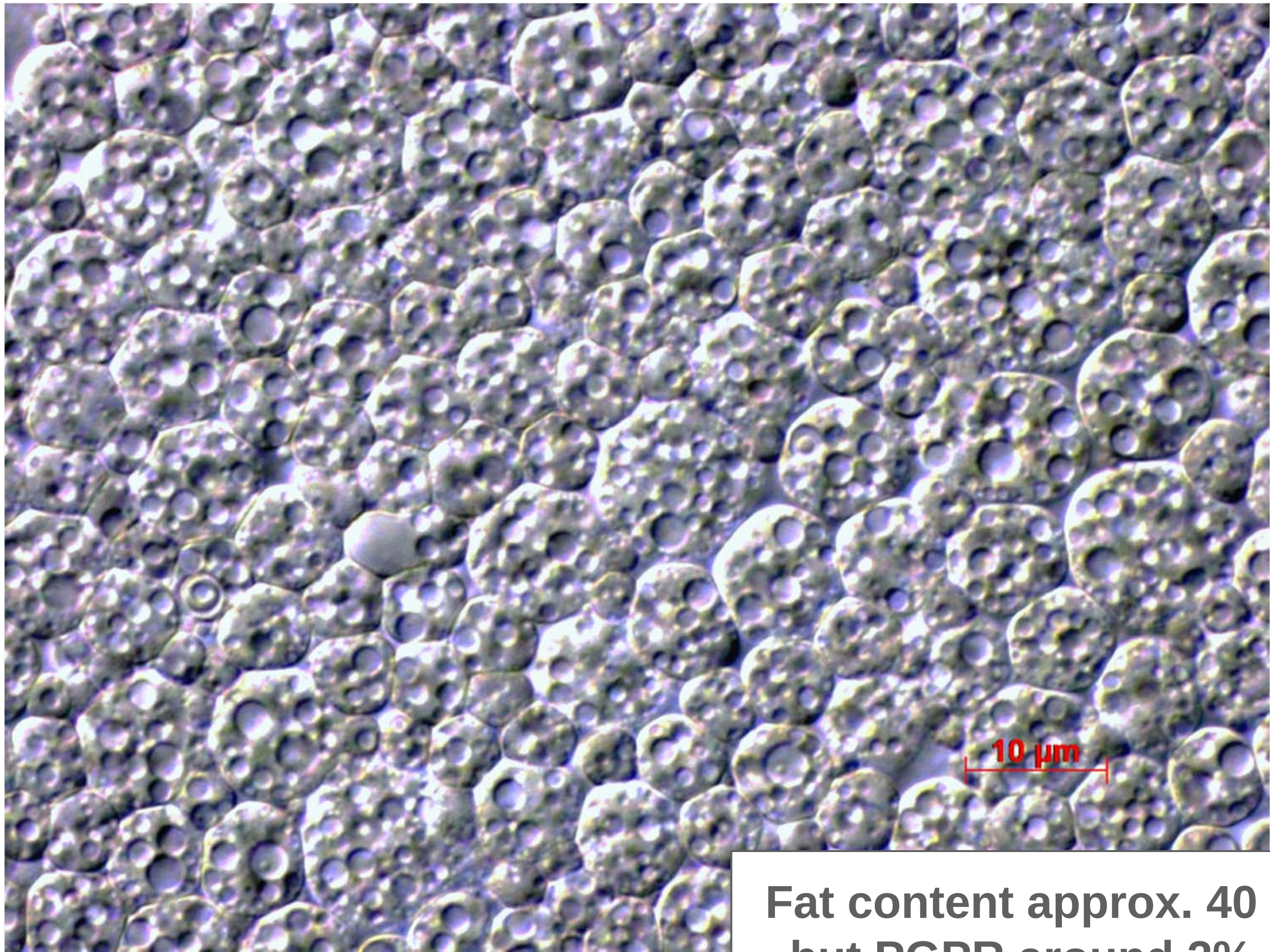
Inner water fully mobile ?



w/o inner emulsions with identical droplet size distribution (0.5 mm)

- apparent self diffusion coefficient of water = 8.3×10^{-12} m^2/s
- still two orders of magnitude larger than droplet mobility

1 year old double emulsion mayonnaise



Fat content approx. 40 % , but PGPR around 2% …

Our conclusions

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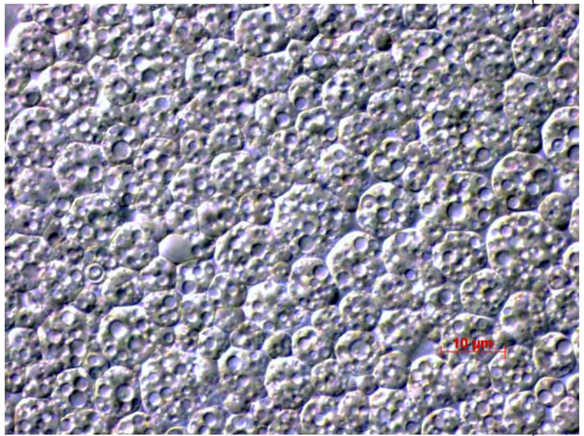
- W/o/w double emulsion approach is applicable to high fat emulsions like mayonnaises
- Sensorial benefits compared to classical low fat technology are real, but do not expect miracles for very low fat contents
- Traditional industrial shelf-life expectations cannot be met with currently available w/o emulsifer (dosing limits)
- Appropriate processing is a must, but it but cannot compensate for lacking emulsifier performance
- Key for improvement are more performant w/o emulsifier solutions



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Thank you for your interest.

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