# The Secret Life of a Pickering Emulsion

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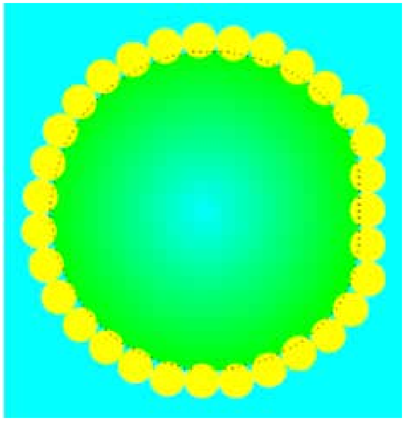
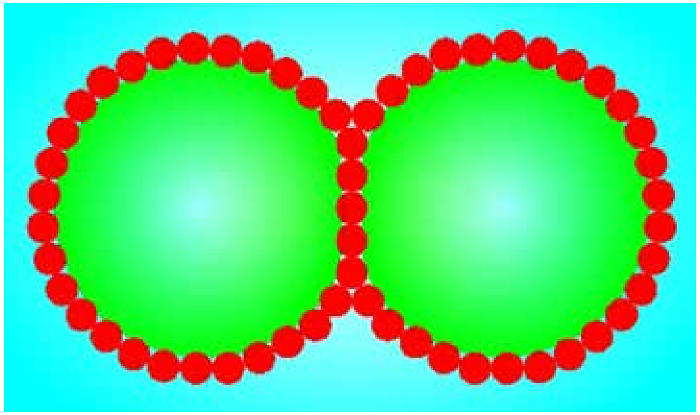
# Outline



1. Pickering emulsions

2. Making & breaking bridges



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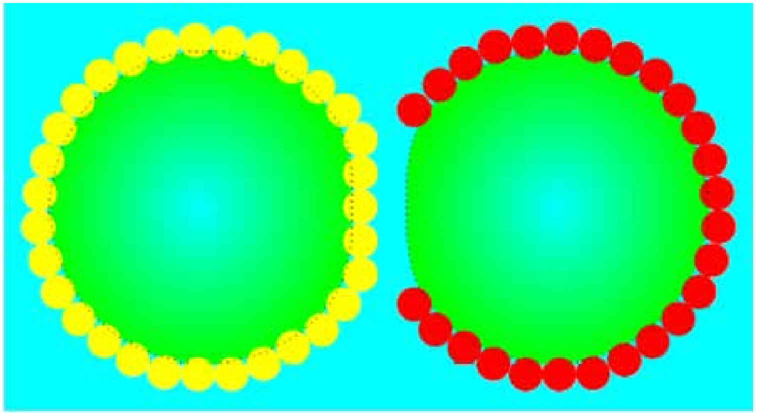
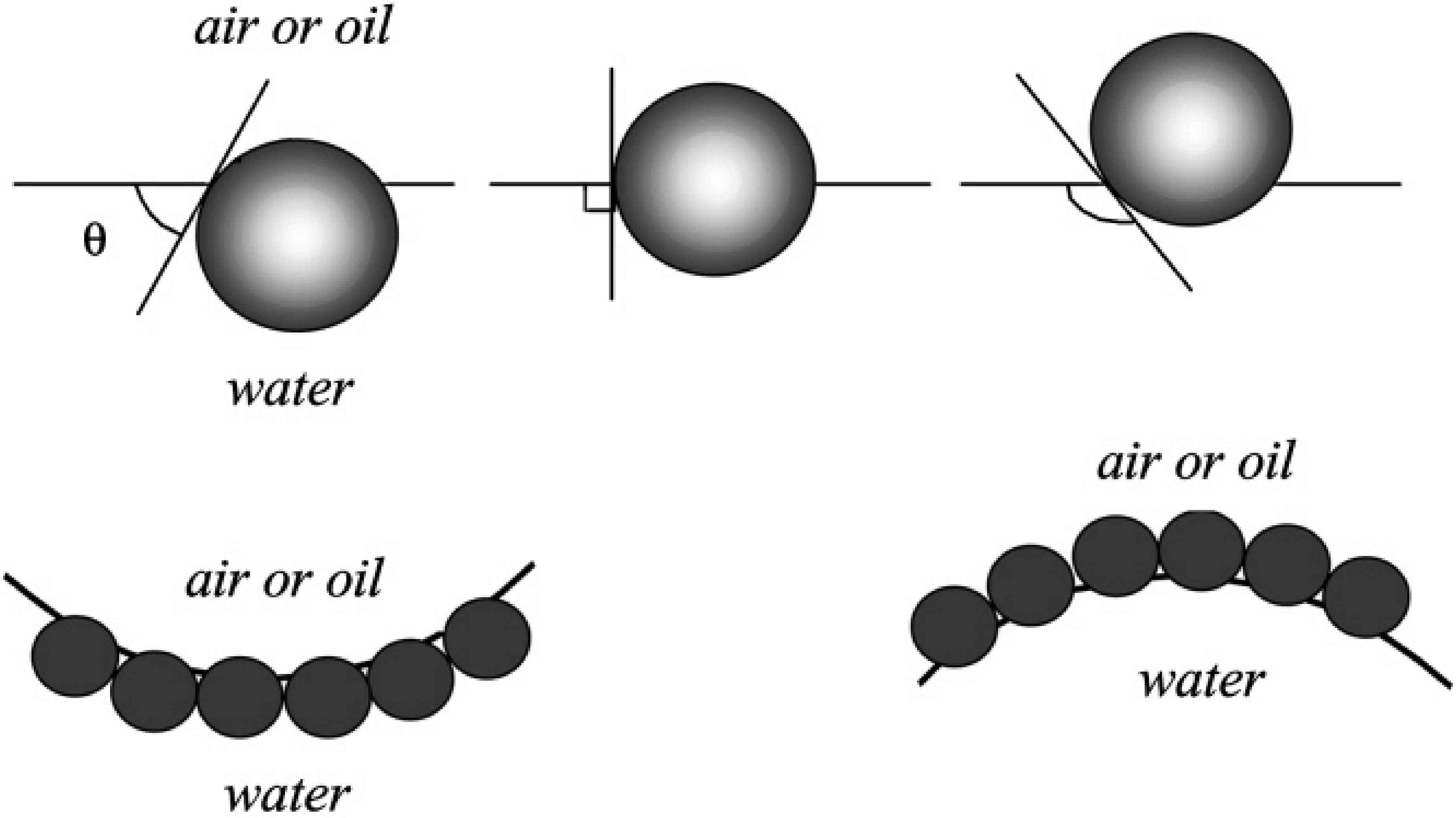


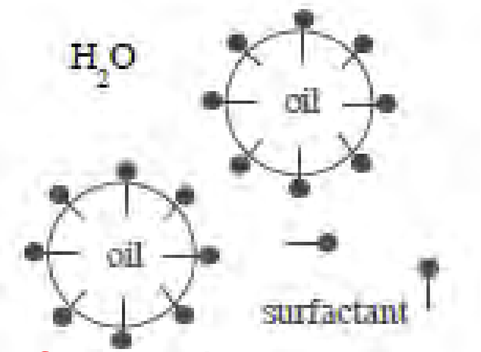
# Particles at liquid-liquid interfaces




B. P. Binks, *Current Opinion in Colloid & Interface Science*, 2002, **7**, 21 –41

# Emulsions

Conventional emulsion



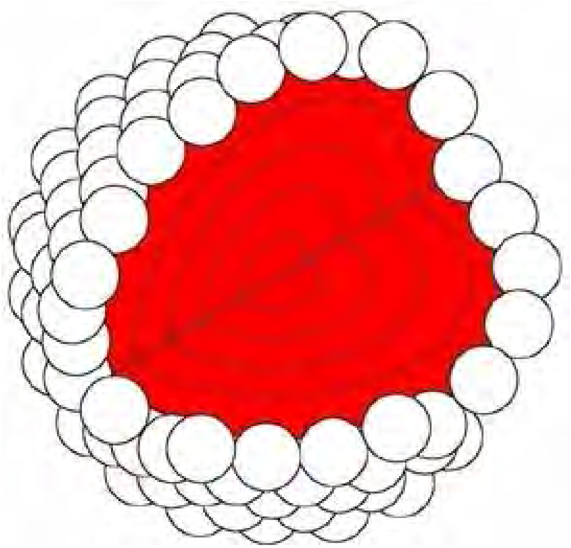

Surface active agent

Trapping energy
$\Delta E \sim k_B T$

i.e. surfactants hop on and off

"Infinitessimal" increase in area is covered by fresh surfactant

γ is decreased



Trapping energy
$\Delta E > 10{,}000 k_B T$

i.e. particles irreversibly trapped

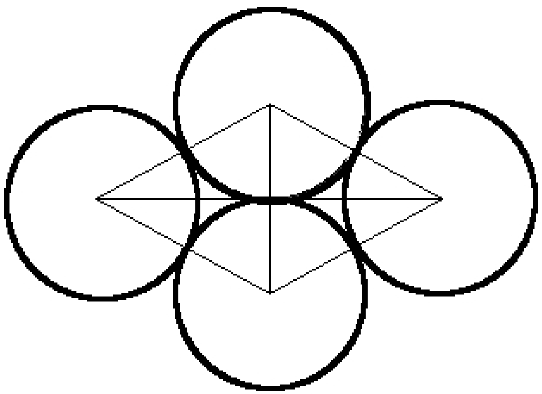
"Infinitessimal" increase in area cannot be covered by mesoscale colloids

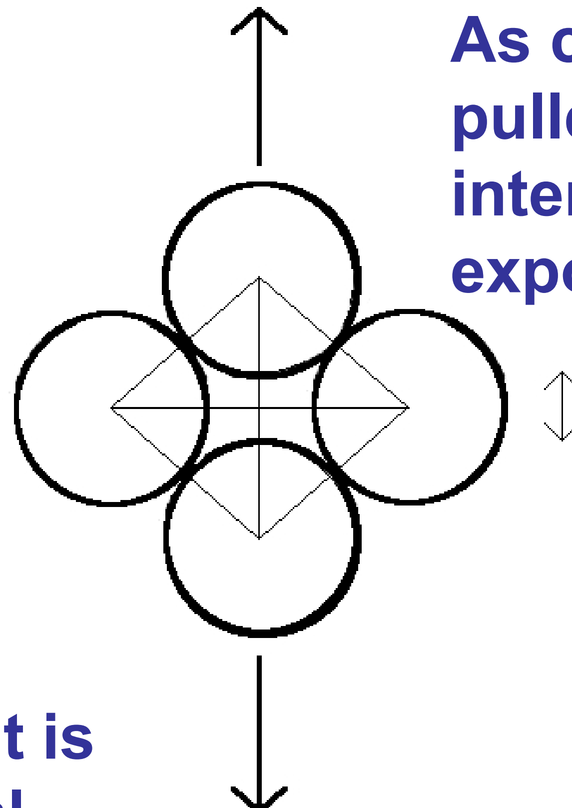
γ unchanged or inappropriate

Pickering emulsion

# Origin of interfacial elasticity

As colloids are pulled apart new interface is exposed





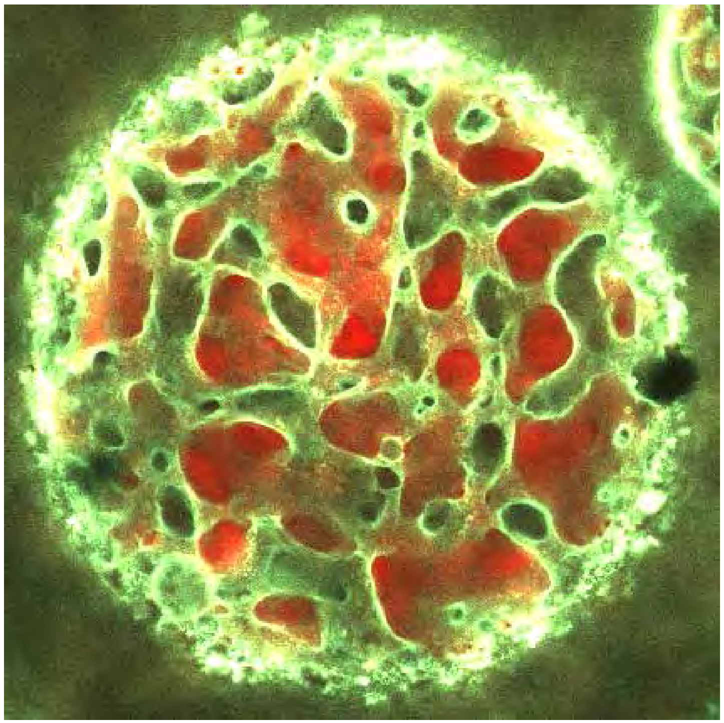
When an interface of close-packed colloids is strained it is predominantly the interfacial tension that leads to the elastic properties.

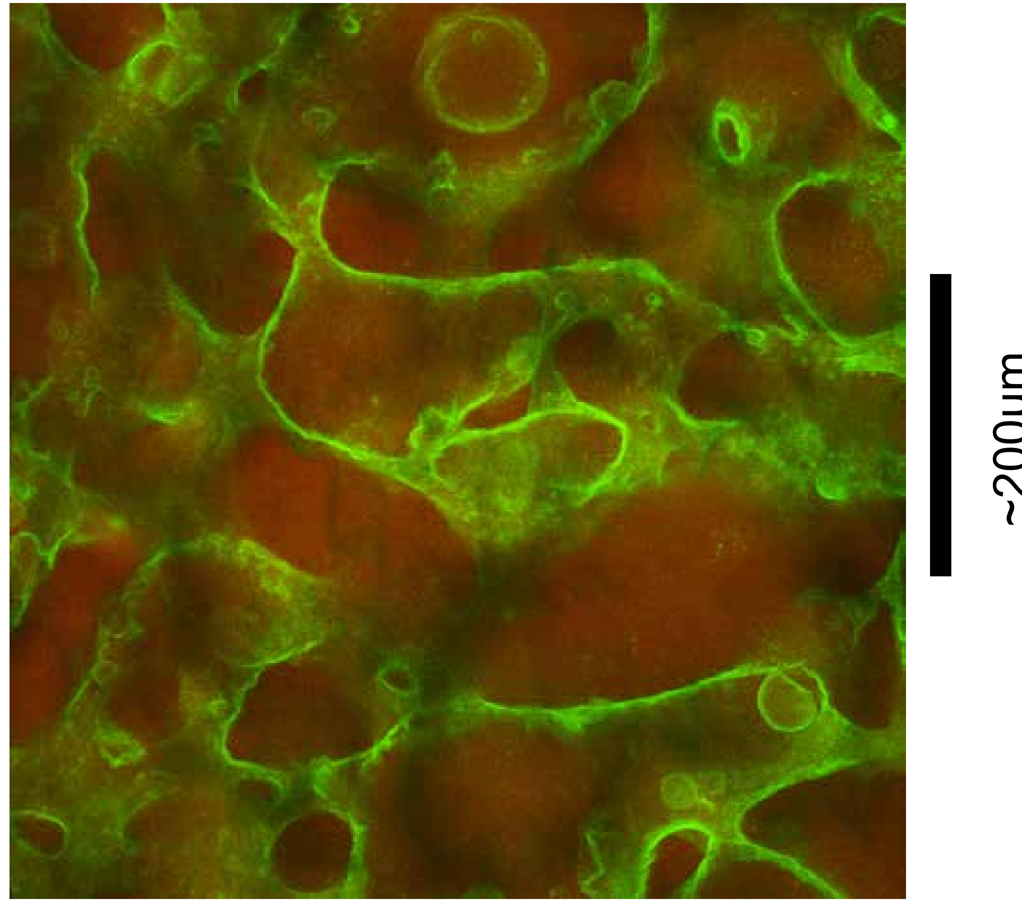
Young's Modulus $E \sim \gamma / d$

D. Vella *et al*, Europhys. Lett. **68**, 212 (2004)

# Bijels: bicontinuous domains

Tavacoli et al Adv. Funct. Mater. **21**, 2020 (2011)






liquids separate via spinodal decomposition

particles *jam* on interfaces

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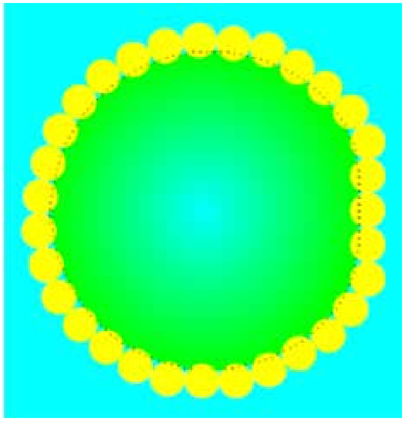

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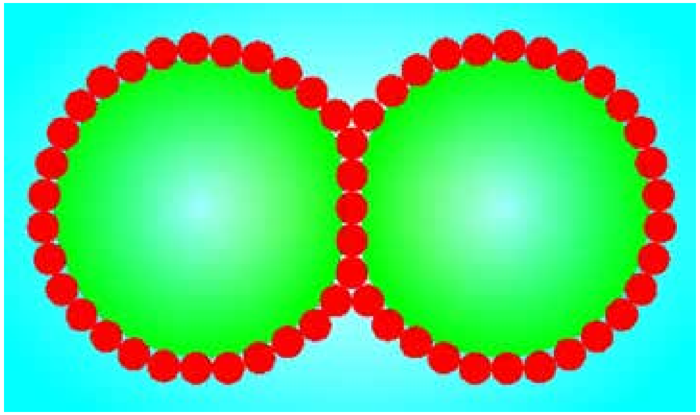

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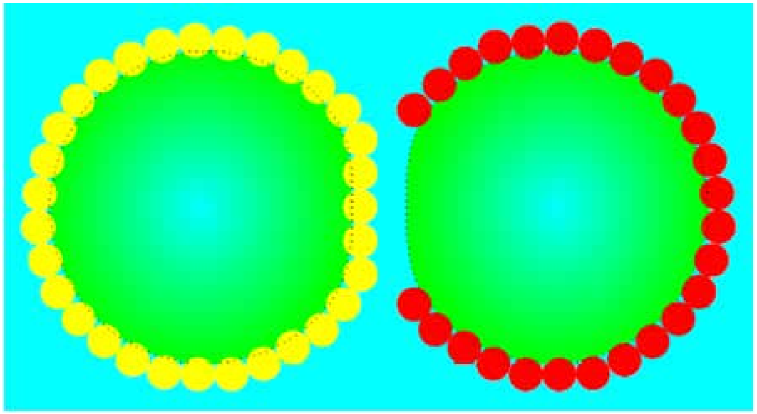
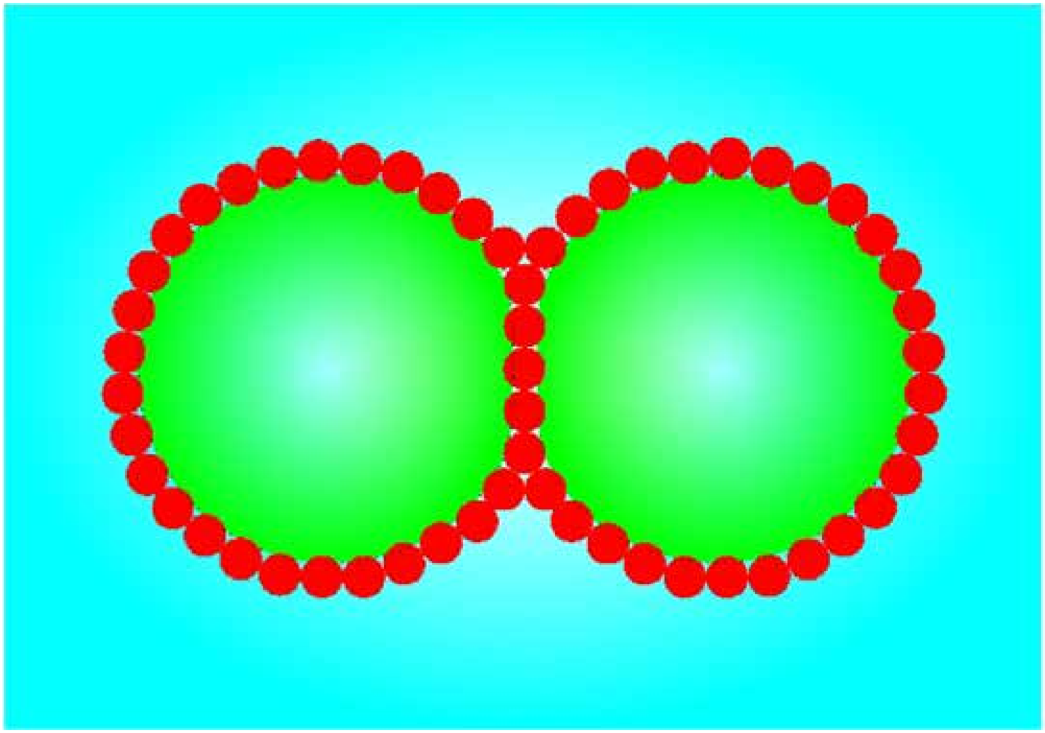
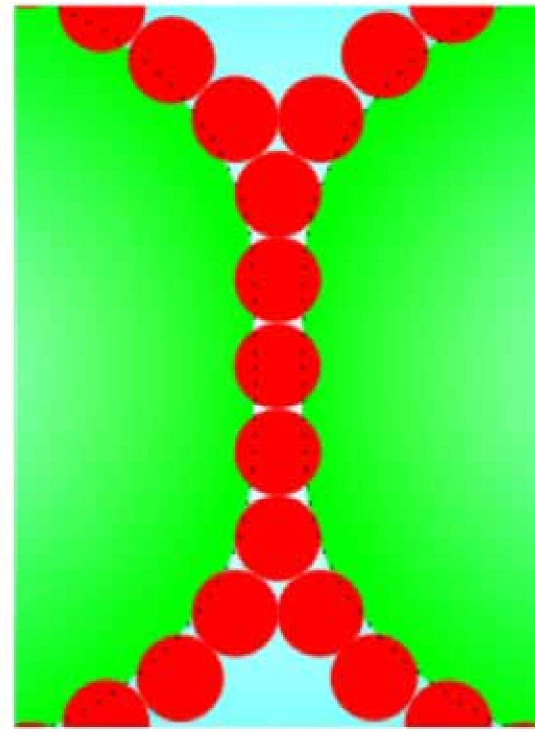


# Colloidal particles are mesoscopic





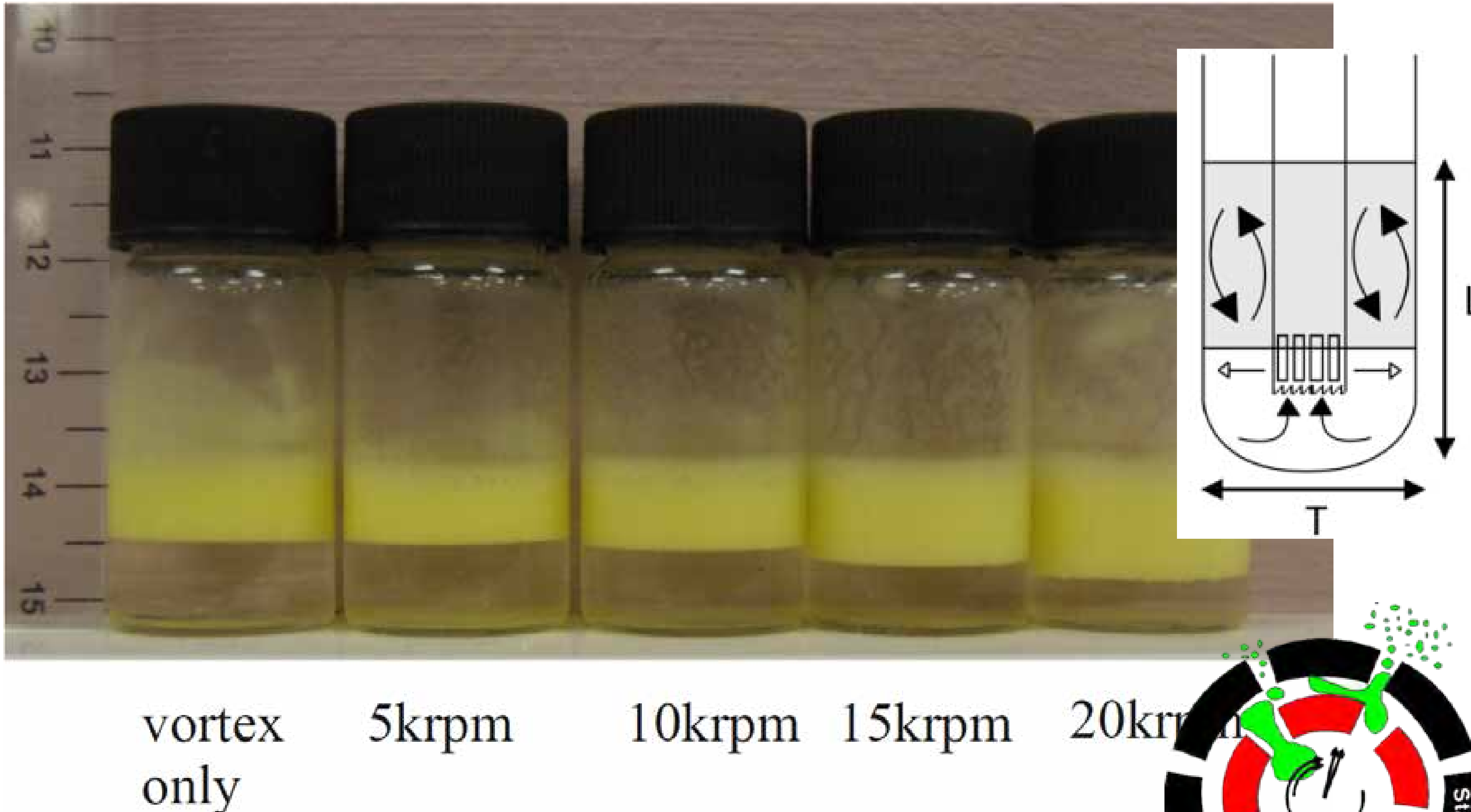
This occurs when:

1. More interface is created than can be protected
2. The shear zone is small compared to the total volume
3. Particle protrude into the continuous phase

# Methods and materials

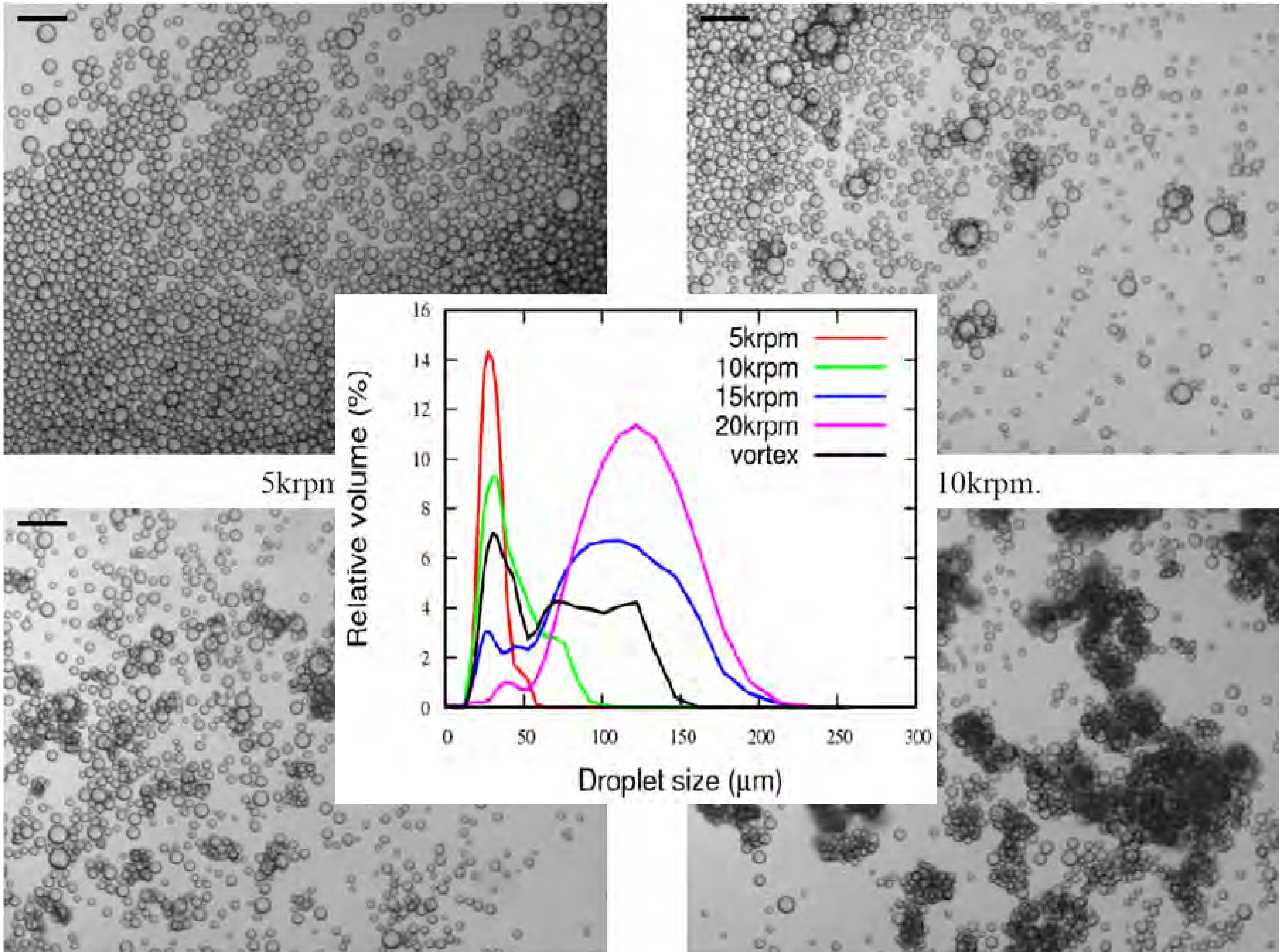
- Oil-in-water emulsions stabilised by Stober silica particles radius ≈ 430nm.
- Oil phase is a mixture of dodecane and isopropyl myristate.
- Disperse particles in water with an ultrasonic probe - typically 150x 1s pulses.
- Vortex mix samples **until clear**.

# Shear rate





34,000 $s^{-1}$



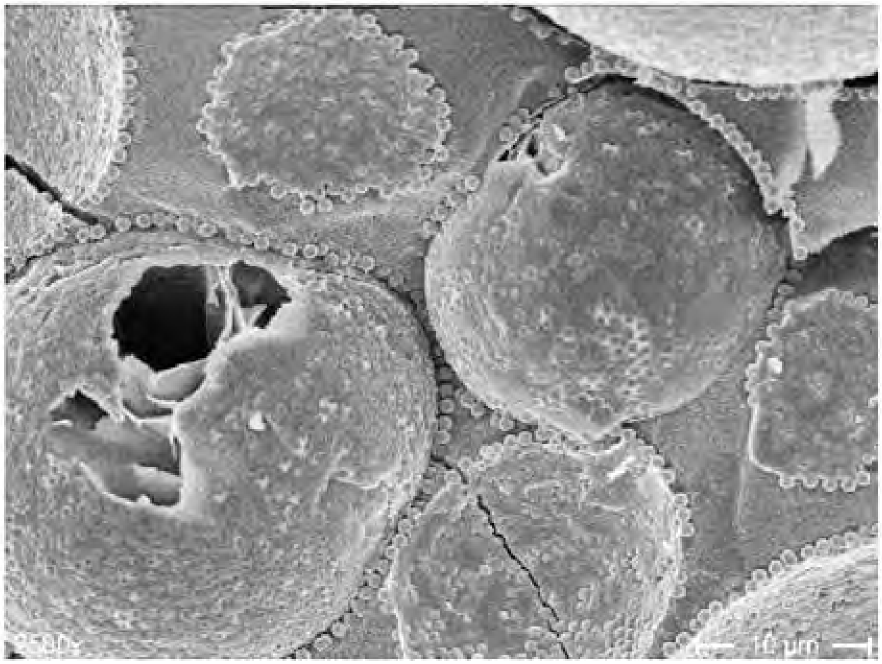

5krpn

10krpm.

15krpm.

20krpm.






SEM shows that particles are indeed bridging droplets.

Also interesting are the hollows left on the droplet surfaces following fracture.

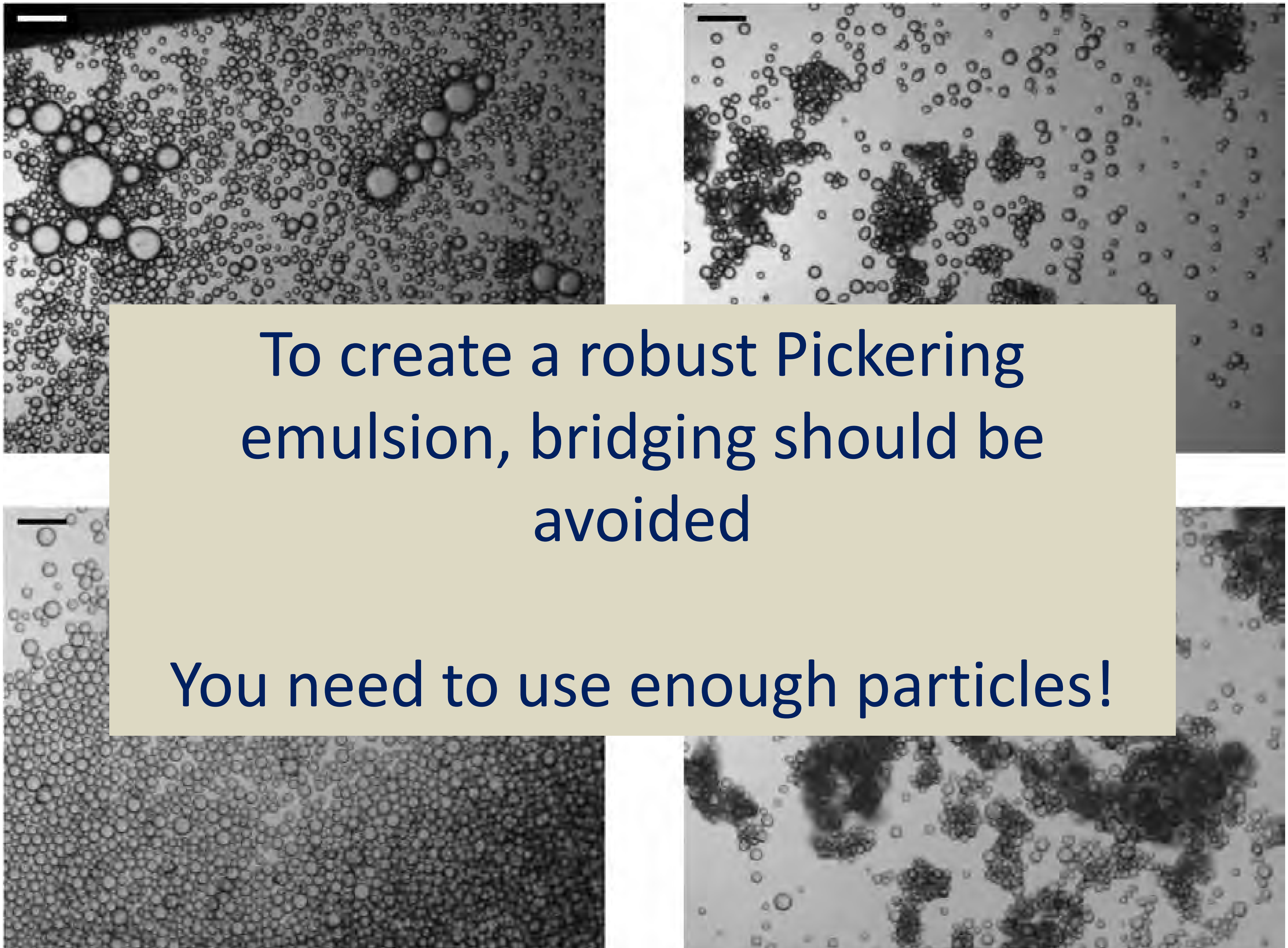
French et al JCIS **441**, 30 (2015)

# Reshearing

| 5krpm then 20krpm | 10krpm | 15krpm | 20krpm then 5krpm | vortex only |
|---|---|---|---|---|

To create a robust Pickering emulsion, bridging should be avoided

You need to use enough particles!



5krpm only.

20krpm only.

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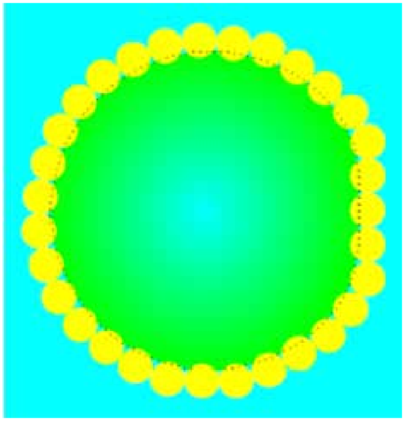

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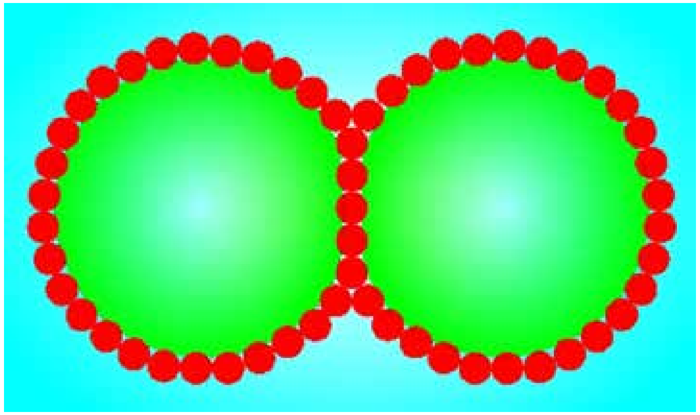

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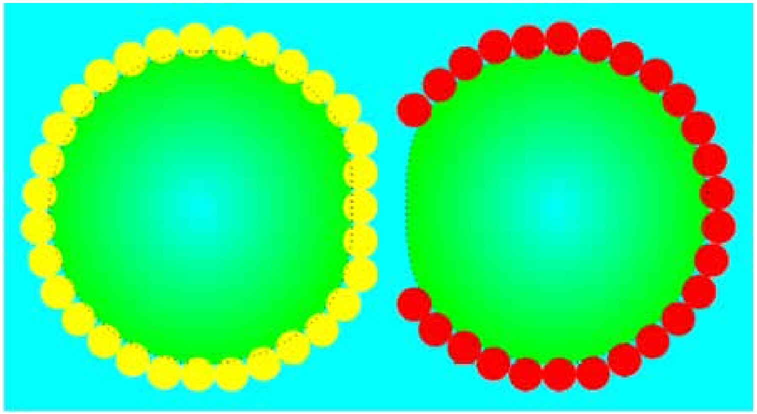
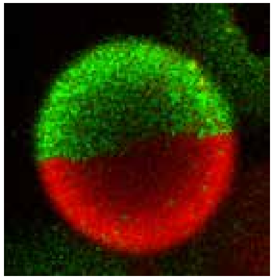
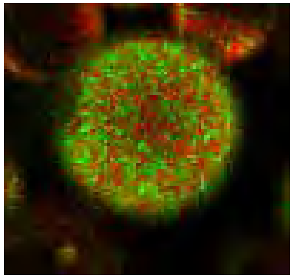


# Materials and Methods

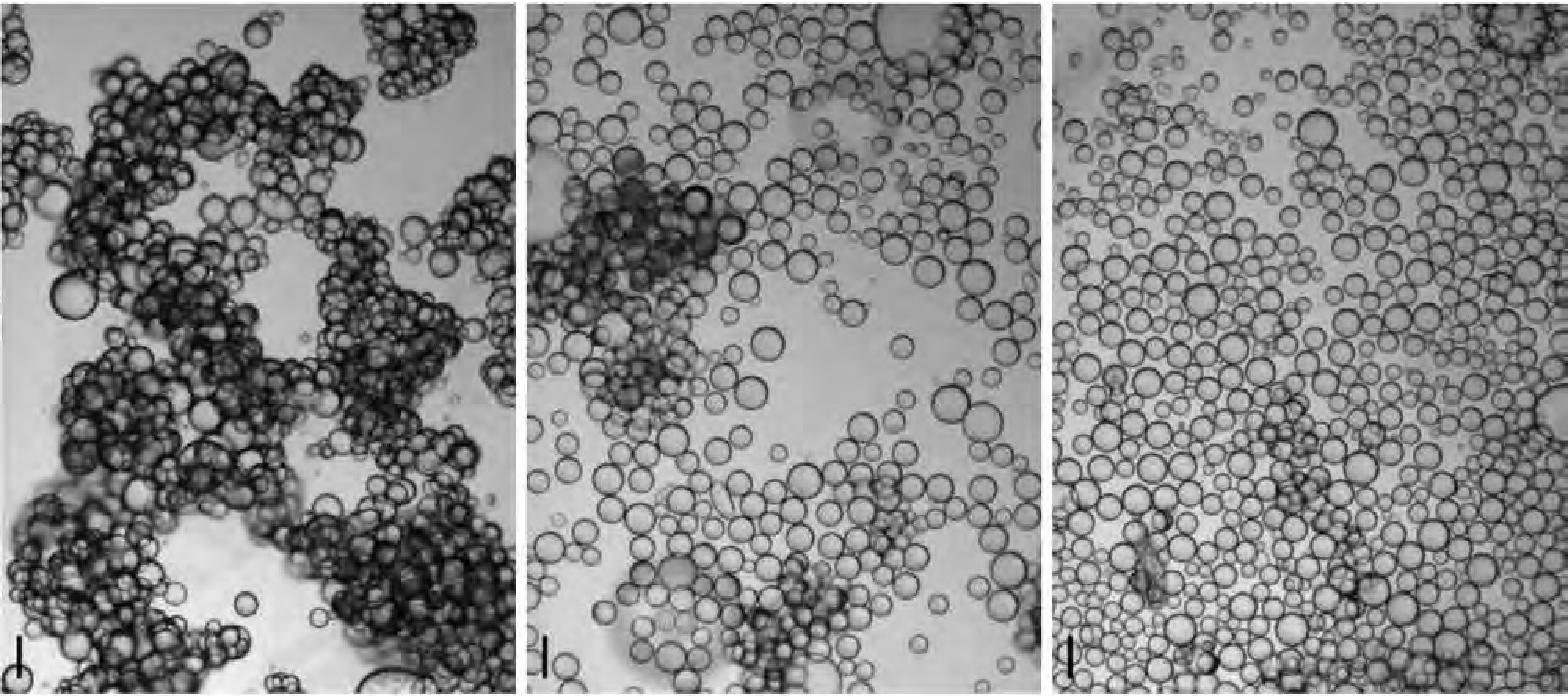
- Initially make two separate emulsions – one red, one green.
- Following emulsification, the red and green samples are mixed together as gently as possible.
- Place on a roller bank:





Shear rate
3 $s^{-1}$

# Bright field microscopy



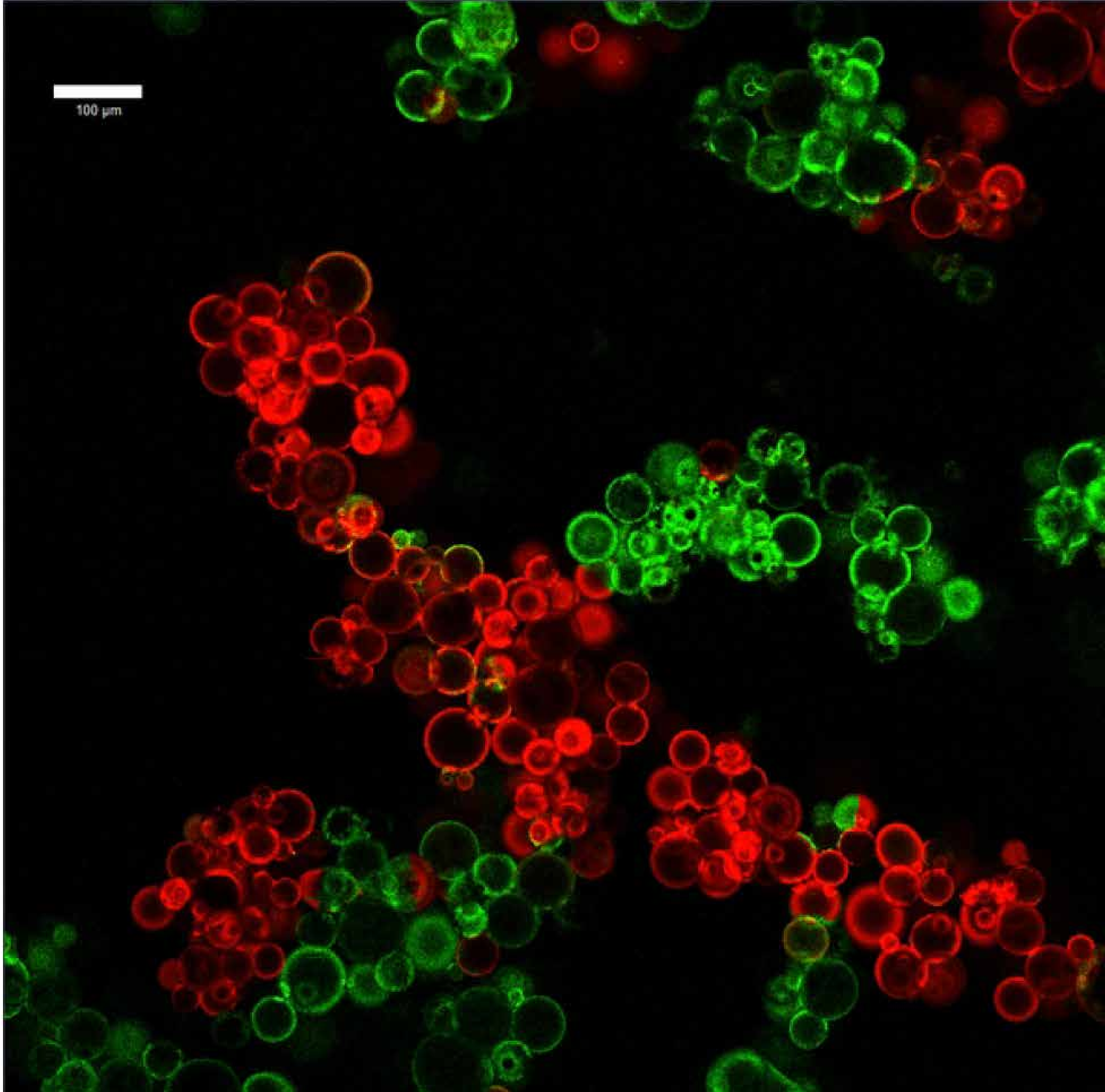
1 h　　185 h　　860 h

As the sample is rolled, the emulsion deaggregates. Scale bars are 100 μm.

100 µm

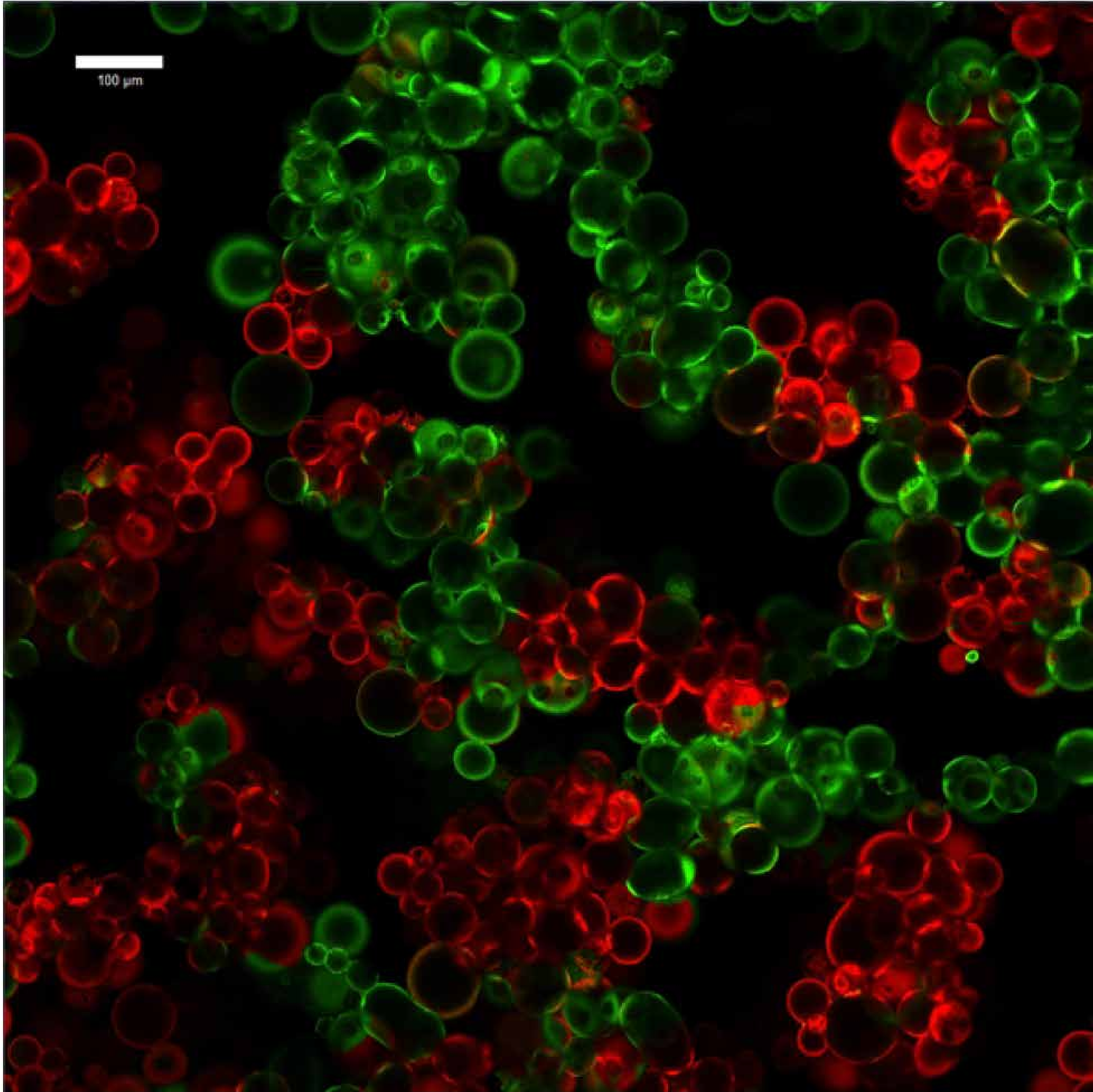
# 1 hour rolling

Colours segregated



100 µm

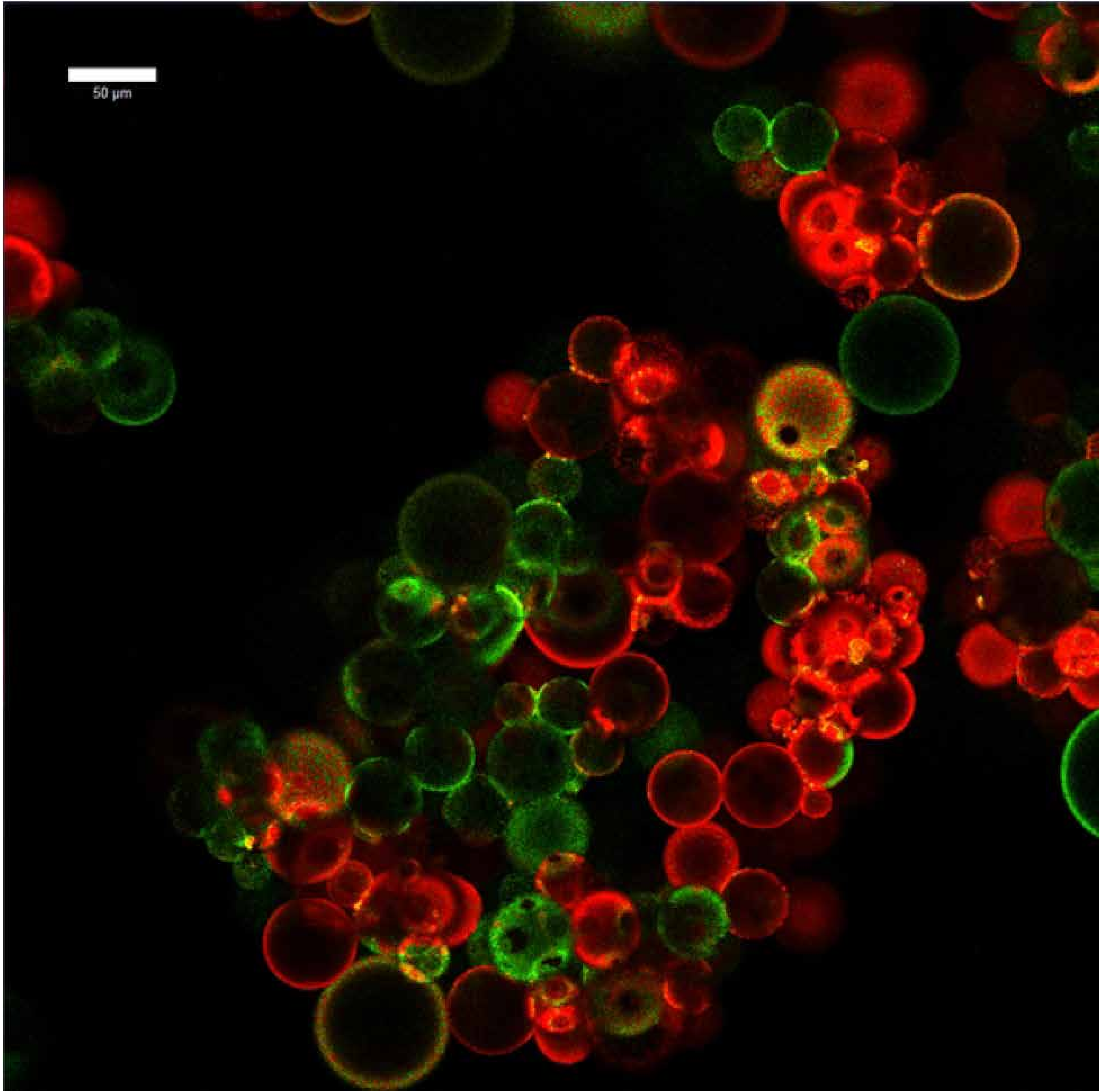
# 6 hours rolling




More interspersed

Some multi-coloured drops

50 µm

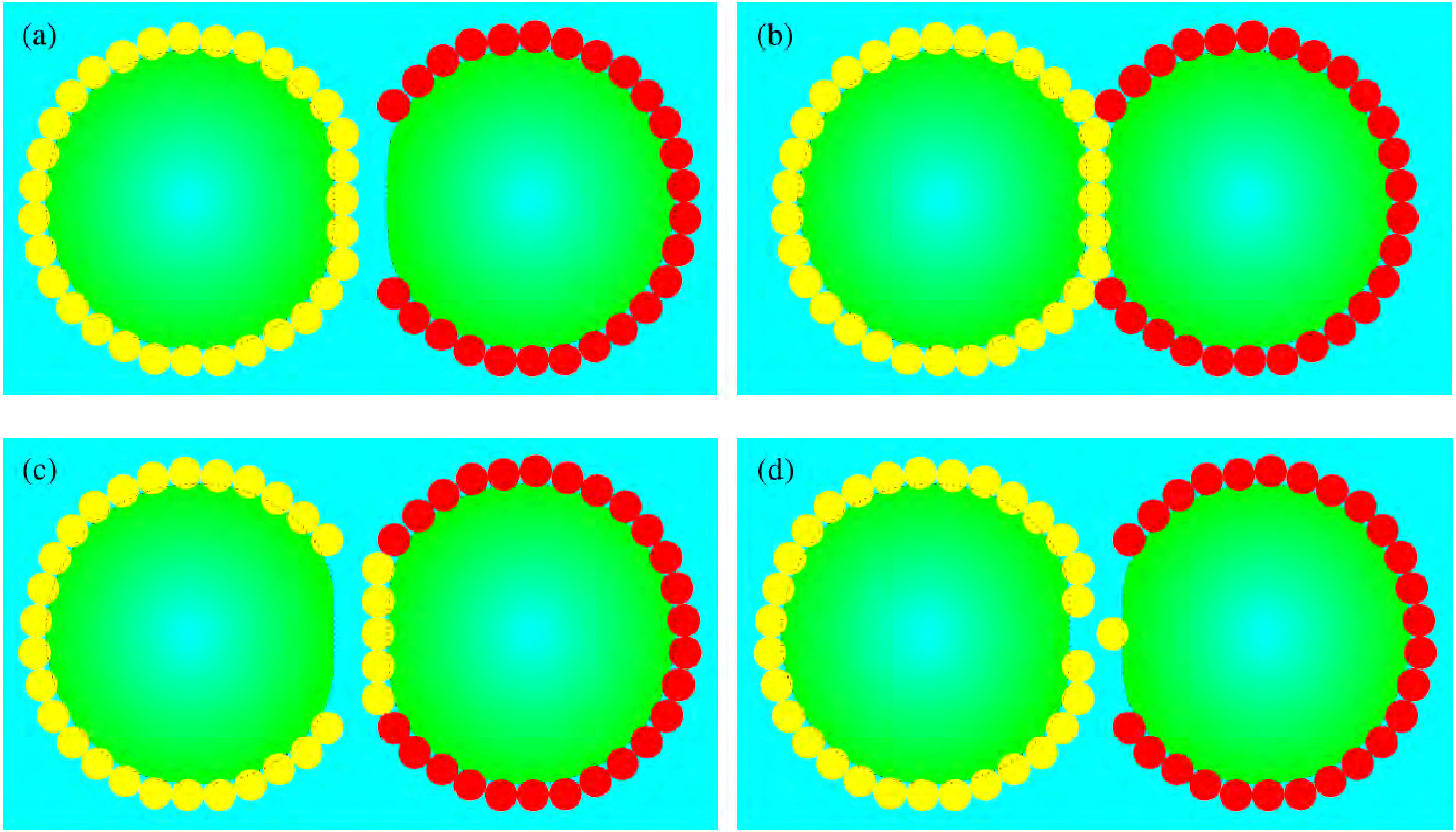



# 21 hours rolling

More thoroughly interspersed

Some well-mixed drops

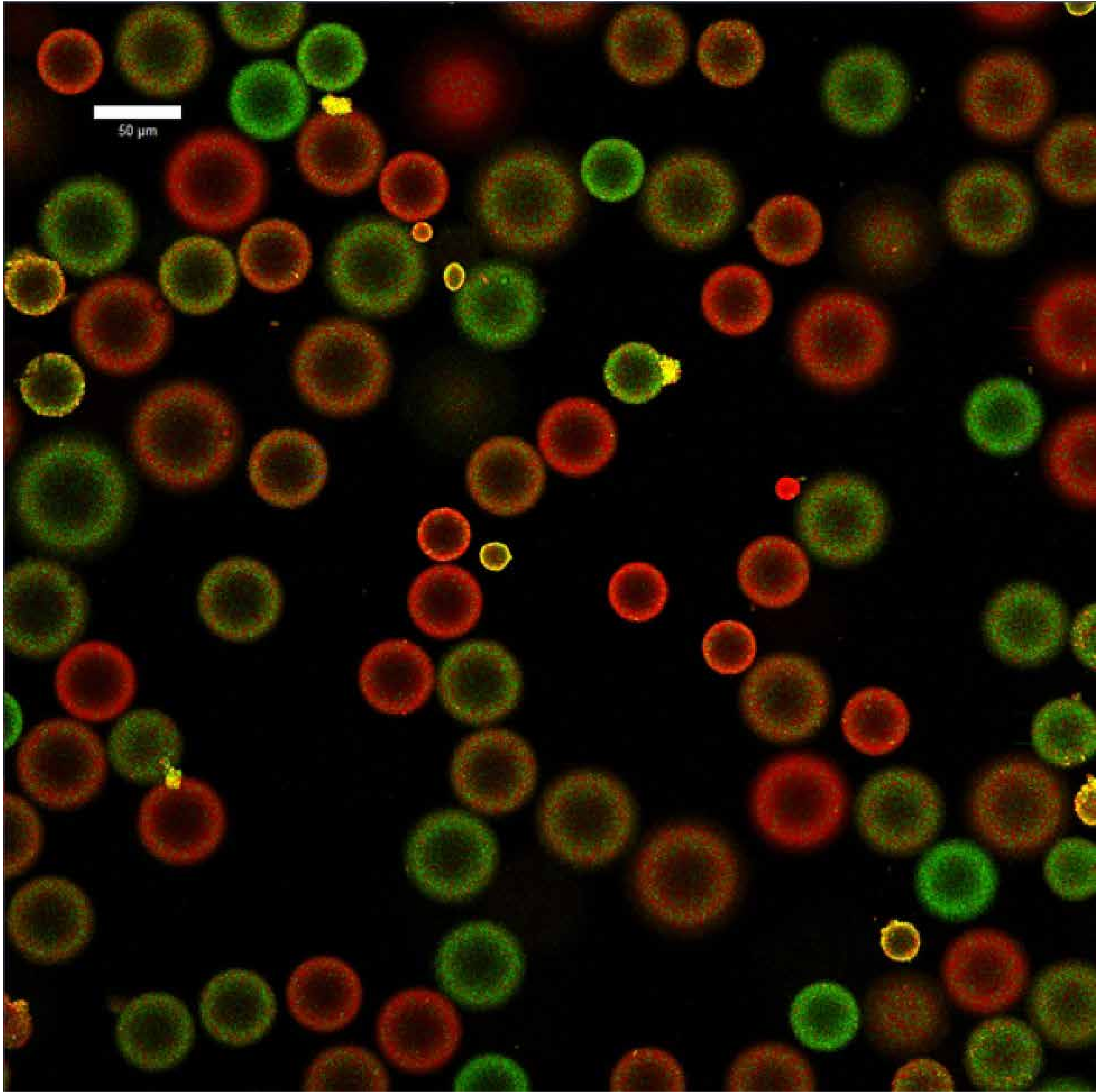
# Mechanism



50 µm

# 1191 hours rolling

All multi-coloured drops



# Acknowledgements

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