The Secret Life of a Pickering Emulsion

Paul S. Clegg
Outline

1. Pickering emulsions

2. Making & breaking bridges

3. The secret life of Pickering emulsions
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
  - \( \gamma \) is decreased

Pickering emulsion

- trapping energy \( \Delta E > 10,000k_B T \)
  - i.e. particles irreversibly trapped
  - “Infinitessimal” increase in area cannot be covered by mesoscale colloids
  - \( \gamma \) unchanged or inappropriate
When an interface of close-packed colloids is strained it is predominantly the interfacial tension that leads to the elastic properties.

Young’s Modulus $E \sim \gamma / d$

As colloids are pulled apart new interface is exposed

Bijels: bicontinuous domains


liquids separate via spinodal decomposition

particles *jam* on interfaces
Outline

1. Pickering emulsions

2. Making & breaking bridges

3. The secret life of Pickering emulsions
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

vortex only  
5krpm  
10krpm  
15krpm  
20krpm  

34,000 s⁻¹
SEM shows that particles are indeed bridging droplets.

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

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

20krpm
To create a robust Pickering emulsion, bridging should be avoided.

You need to use enough particles!
Outline

1. Pickering emulsions

2. Making & breaking bridges

3. The secret life of Pickering emulsions
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

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

1 hour rolling

Colours segregated
6 hours rolling

More interspersed

Some multi-coloured drops
21 hours rolling

More thoroughly interspersed

Some well-mixed drops
Although the forces are gentle, the torques can be quite large.
1191 hours rolling

All multi-coloured drops
Acknowledgements

- David French
- Phil Taylor (Syngenta, UK)
- Jeff Fowler (Syngenta, USA)
- Andrew Schofield
- Joe Tavacoli
- Kathryn White