Mixing Time, Inversion and Multiple Emulsion Formation in a Limonene and Water Pickering Emulsion

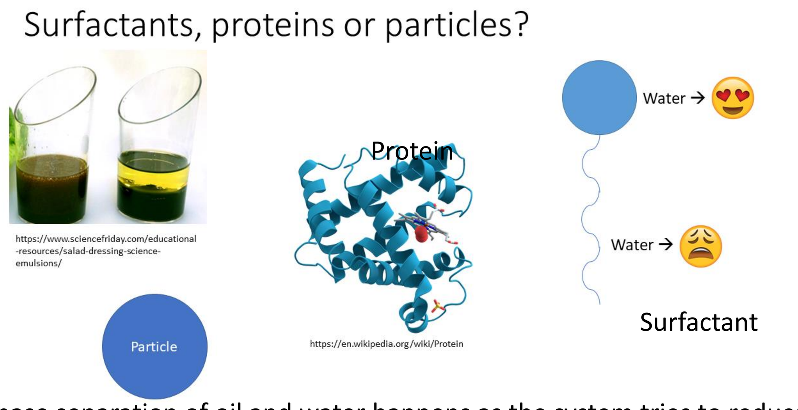
Laura Sawiak[1], Katherine Bailes[2], David Harbottle[2] and Paul Clegg[1]

[1]School of Physics and Astronomy, University of Edinburgh, Edinburgh, United Kingdom

[2]School of Chemical and Process Engineering, University of Leeds, Leeds, United Kingdom

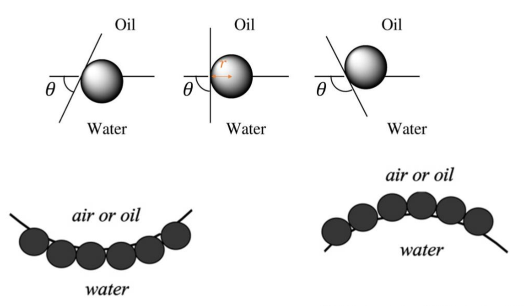
1) Background

Surfactants, proteins or particles?



Three main ways of stabilising an emulsion exist: using surfactants, proteins or particles. Here we focus on particles.

Phase separation of oil and water happens as the system tries to reduce its energy. The interface between oil and water is energetically expensive, so the system acts to reduce its area.

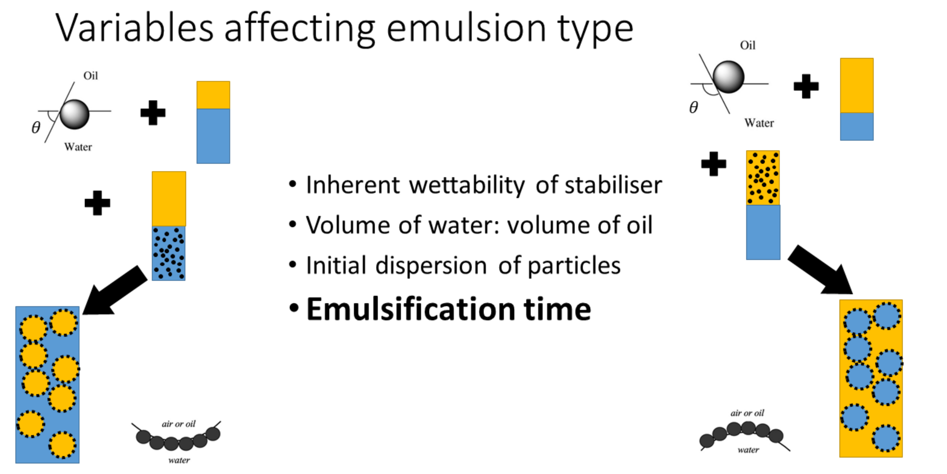


It is possible to predict emulsion type from the contact angle of the stabilising particle.

As the system tries to reduce its energy, a lateral force is applied to the particles on the interface. This leads to an inherent curvature.

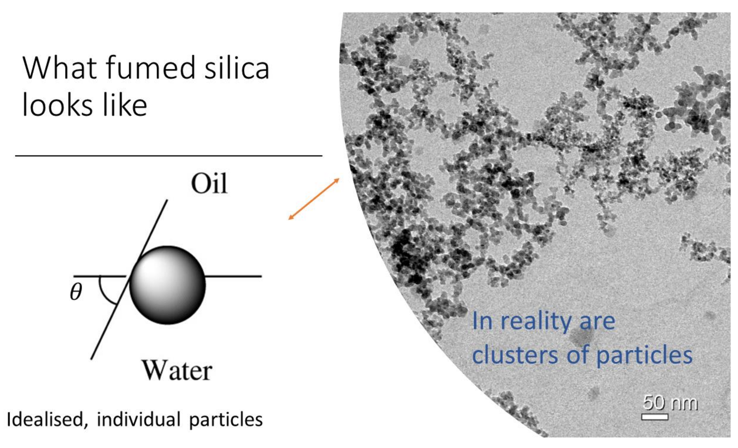
The churning of cream transforms it from a fat-in-oil emulsion to butter, a water-in-fat emulsion. This is shown in the micrographs. Bottom left: red fat in green oil. Bottom right: black water in green oil.

Variables affecting emulsion type



- Inherent wettability of stabiliser
- Volume of water: volume of oil
- Initial dispersion of particles
- **Emulsification time**

What fumed silica looks like

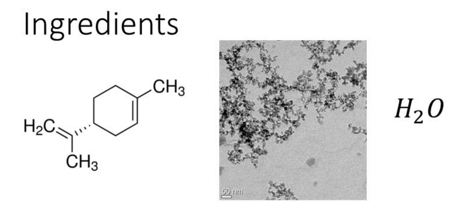


The above theory implies separate particles. Fumed silica is more complicated than that, however. It consists of small primary particles which are aggregated into bigger structures.

2) Emulsification

The ingredients are just limonene, water and the stabiliser. Predispersing the particles influences the resulting emulsion type.

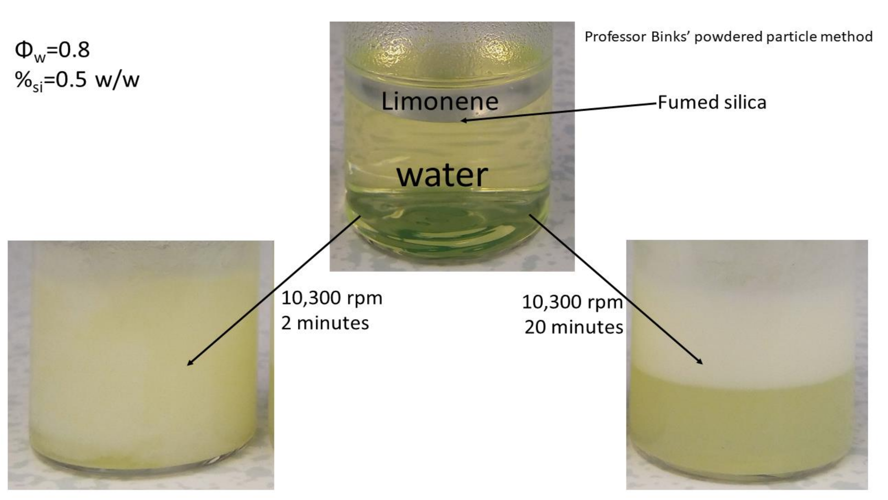
Ingredients



Where you put the particles to begin with is important!

Rotor Stator

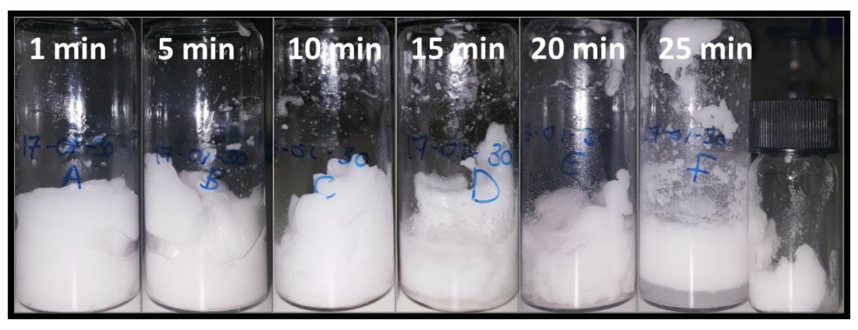
Φ_w=0.8
$\%_{si}$=0.5 w/w



Mixing the same composition for different amounts of times leads to completely different emulsions with different flow properties. This emulsion is mostly water by volume so we see that the droplets undergoing this transformation are water-in-oil

3) Phase inversion

Phase Inversion with mixing time



Φ_w=0.8
$\%_{si}$=0.1% w/w

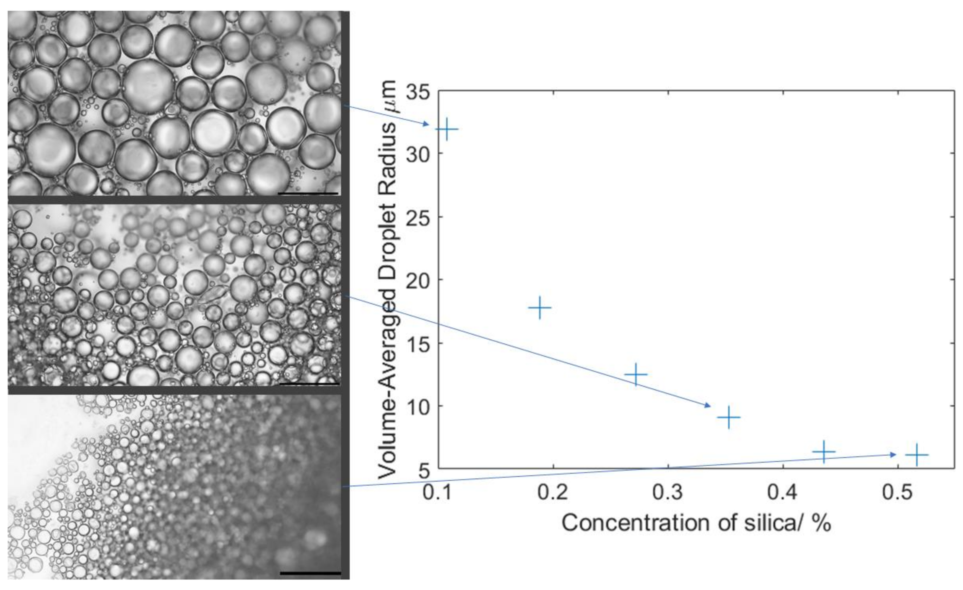
Stabiliser = partially hydrophobized fumed silica
Oil = limonene

A set of five emulsions were made with the same composition but varied emulsification time. The water was dyed with Nile Red at a concentration of 2.1 μM.

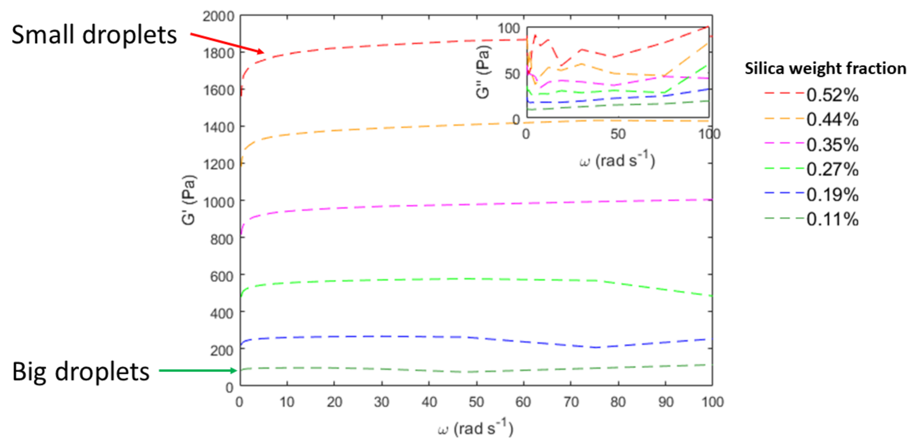
These emulsions are looked at in more detail in the microscopy section. In order to fully understand the micrographs it is helpful to look at the accompanying rheology results first, shown below.

4) Rheology

The rheology experiments were all done using a couette-cup geometry. The emulsions examined were not the ones above, showing phase inversion. Instead a simpler system was examined with predispersed silica. This allowed us to separate the effects of lumps of particles and droplet sizes on the resultant rheology. The aim was to see how different droplet sizes flow.

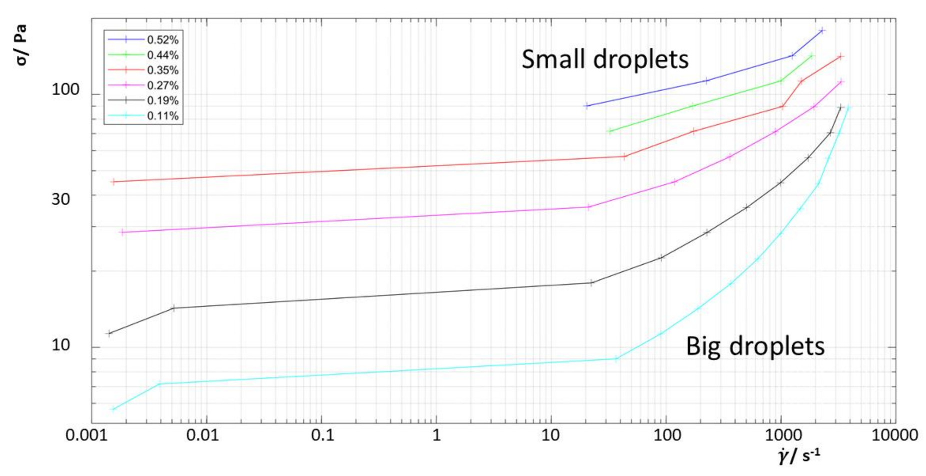


A range of water-in-oil emulsions were made up with different size distributions by controlling the silica concentration. This was done by diluting a stock dispersion of silica-in-oil. These emulsions had the advantage of no particle clusters present.



Data collected with Kat Bailes[2]

Oscillatory rheology showed that the storage modulus (G') is dominant, particularly for small droplets. This tells us that they are elastic, and as such are hard to deform and flow.



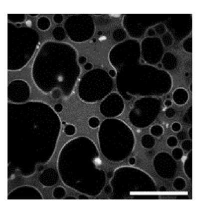
Data collected with Kat Bailes[2]

Flow curves confirm that smaller droplets are much less flowable than large droplets. This is seen through the larger viscosities and yield stresses of the smaller droplets.

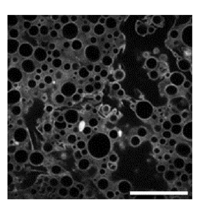
Big droplets flow more easily.

Conclusion

Uniting emulsification experiments with rheology

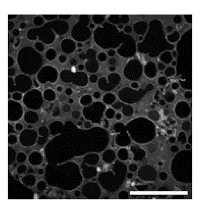


Some distribution of droplets forms, with clusters of droplets

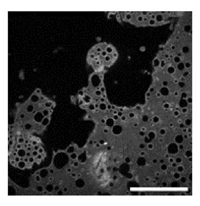


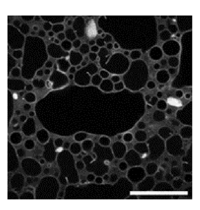
As floppy interface of big droplets bend, bare patches on the interface form rendering them weak

All droplets get smaller

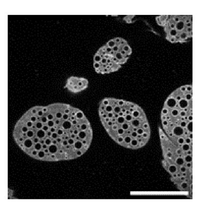


Big droplets coalesce and small droplets jam within the oil phase





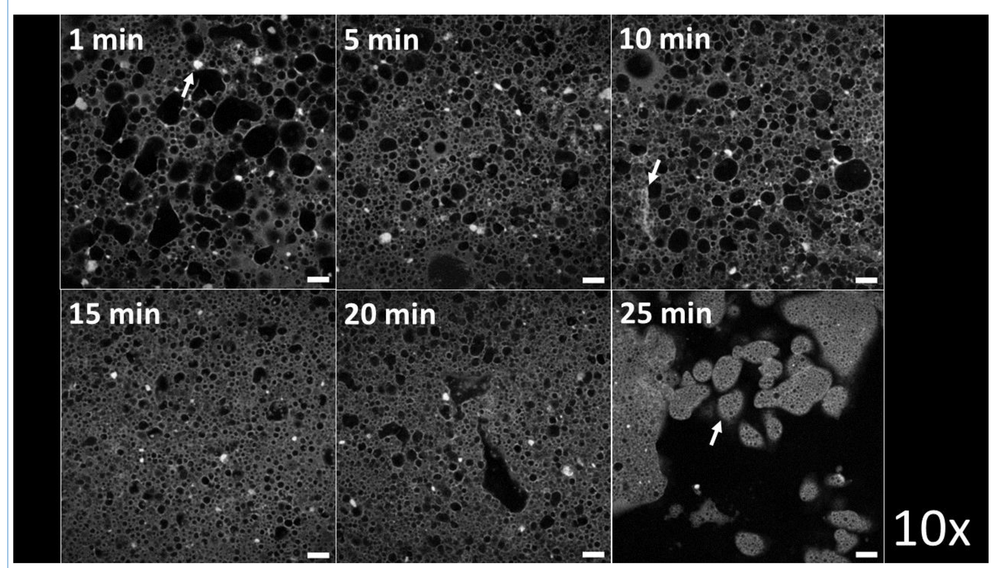
Small droplets non-deformable; big droplets deform and mix



System inverts to a high internal phase emulsion!

This phase inversion is due to differing flow properties between big and small droplets! (and not due to clusters of particles)

5) Microscopy



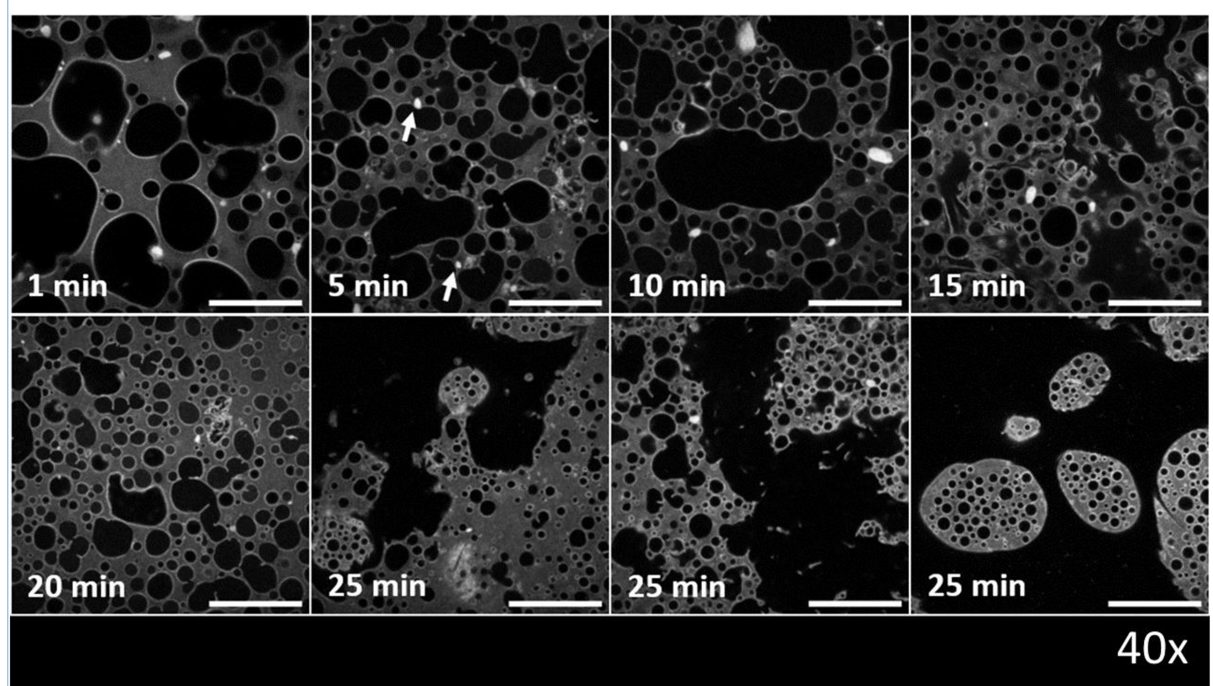
Confocal fluorescence microscopy allows the water (black), limonene (grey) and silica (bright white) to be visualised

The arrows point to a silica cluster, an elongated silica structure and a multiple emulsion droplet respectively.

Droplet shapes and sizes vary with mixing time. The times in the corner of each panel reflect the mixing time for that sample. At low emulsification times, there are bare patches upon the interface, allowing arrested coalescence to occur. As such, there is a distribution of small droplets, and larger, coarsened droplets. At later times, the gap between small and large droplets reduces until the 20 minute panel, where a large, irregularly shaped droplet can be seen.

As all droplets become smaller, their elasticity increases, as shown in the previous section. This means larger droplets are easier to flow, and they squeeze through tight gaps. As the interface deforms, the local concentration of stabiliser upon the interface is reduced, rendering them weaker. This allows selective coalescence of larger droplets, leading to the phase inversion.

As the interface folds, a small number of elongated silica structures form such as that shown in the 10 minute panel. All scale bars are 100 μm.

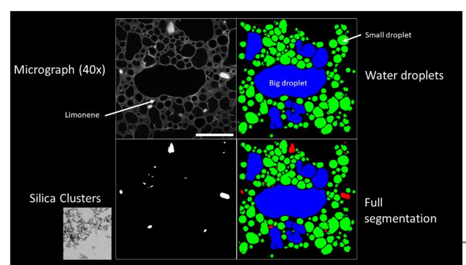


Looking at a higher magnification, the interfaces of droplets can more accurately be seen. The density of silica at the interface is reflected by its brightness, Silica clusters, as pointed to by arrows, can be stuck to the interface of droplets or be in the bulk oil phase. Notably, at 10 minutes, a large droplet is seen to be deformed by a group of smaller, more spherical droplets.

In the first 25 minute panel, a pinch-off event can be seen, where a group of water droplets in oil are about to break off into a multiple emulsion droplet.

At 25 minutes the phase inversion is complete. As can be seen from the multiple emulsion droplets of water-in-oil-in-water.

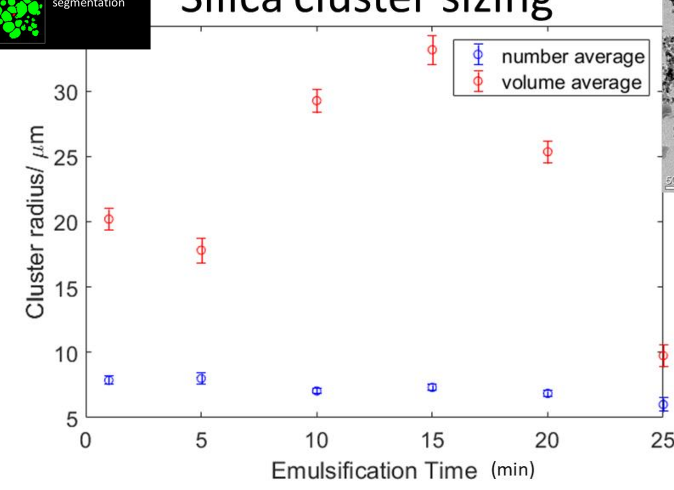
6) Statistics

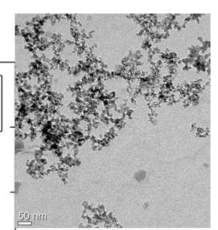


Left: matlab was used to segment the micrographs to get quantitative data for analysis. Large and small droplets were separated by a 20 micron radius threshold.

Silica cluster sizing

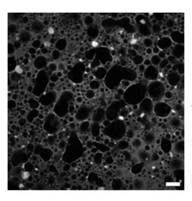
The number average is the unweighted mean, and the volume-average is the average where each cluster is normalised by its size. This means larger clusters affect the resulting number more.

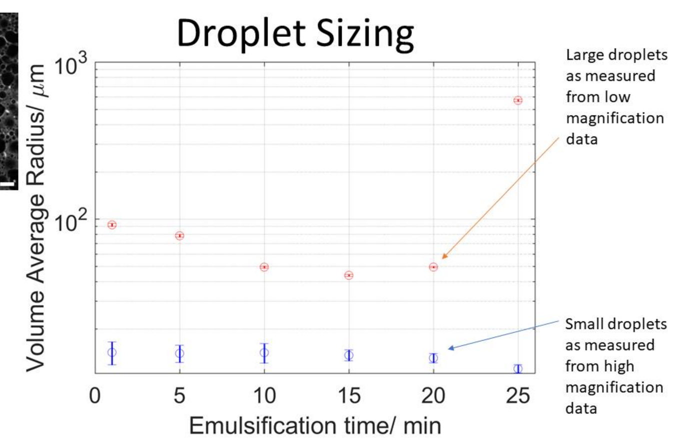




The size normalisation of silica clusters matters. On average clusters are broken up. However, a small number of large, less dense clusters from as the interface of floppy, large droplets folds upon itself. This is reflected by the increase of cluster size when weighting the average by cluster volume

Droplet Sizing





The evolution of large and small droplets can be seen in this graph. The small droplets get slightly smaller with time whereas the large droplets get smaller before growing and becoming the continuous phase, completing the phase inversion.

EPSRC
THE UNIVERSITY of EDINBURGH
SUPA
SOFI CDT