

BIJEL CAPSULES



J.W. Tovacoli, E.M. Herzig, and P.S Clegg

Institute for Condensed Matter and Complex Systems

and

The Edinburgh Complex Fluid Partnership

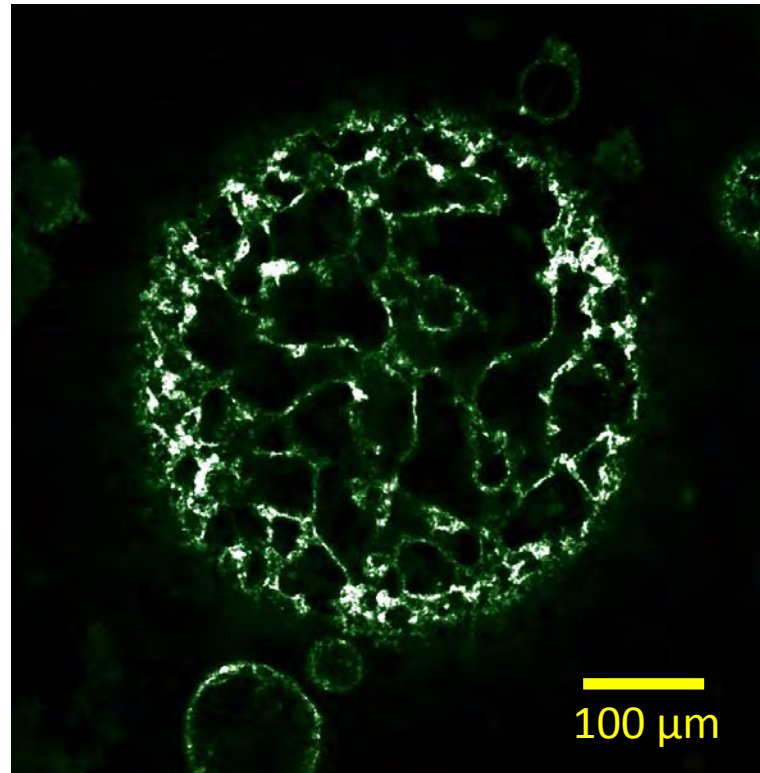
School of Physics, University of Edinburgh



Bijel Capsules: Road Map



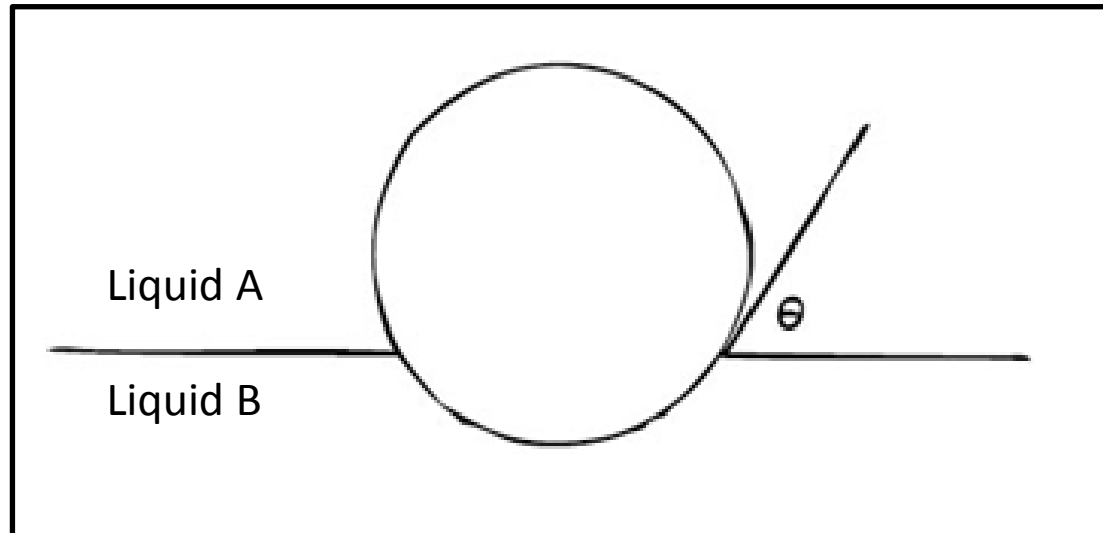
- Colloidal particles as interface stabilisers
- Bijels
- Bijel capsules



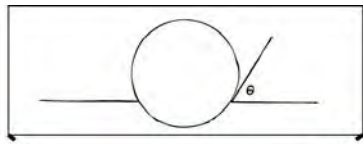
Particles at Interfaces

$$\Delta E = \pi r^2 \gamma_{ow} (1 - |\cos \theta|)^2$$

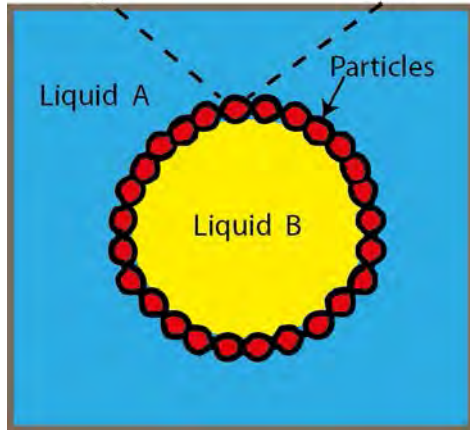
$$> 10\,000 k_B T$$



Solid-Stabilised Capsules

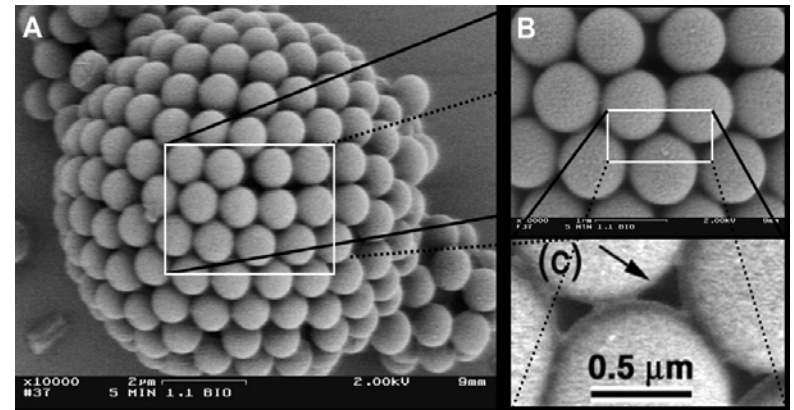


Particle Stabilised Emulsions

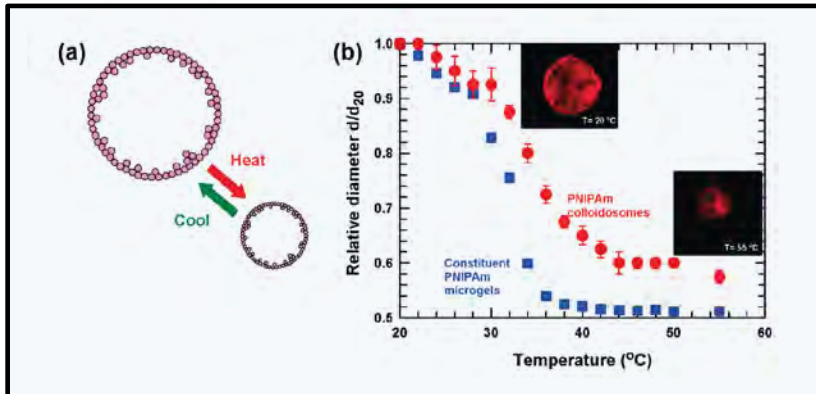


Discovered by Ramsden and Pickering (independently)

Colloidosomes



P-NIPAM based capsules



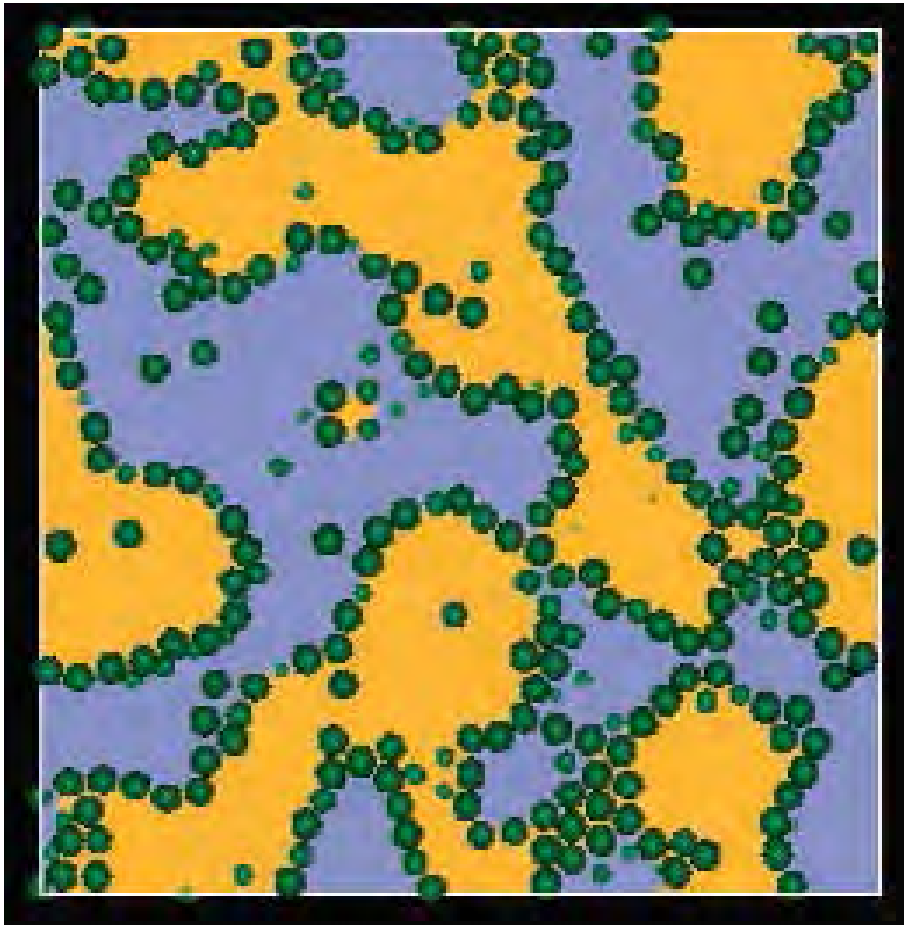
D. Dinsmore et al. Science 298, 1006, (2002)

Shah et al. Langmuir 26(3) 1561 (2010)

Bicontinuous Interfacially Jammed Emulsion Gel

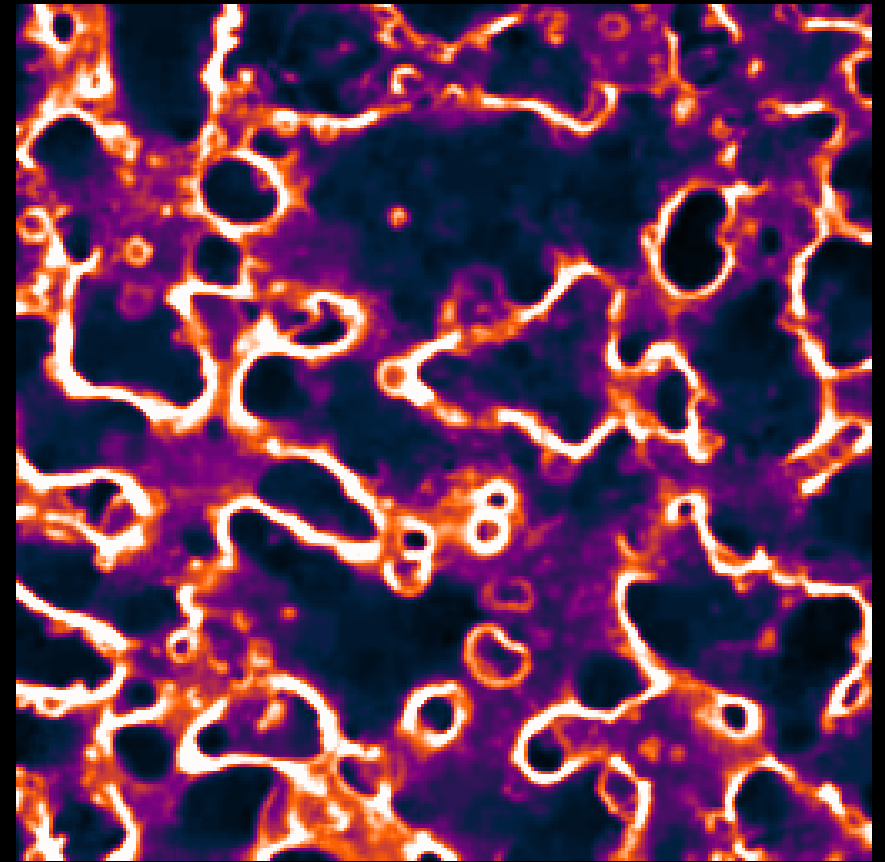
2 liquid domains stabilised by adsorbed particles
Domains tortuous and entwined

The first bijel: water, lutidine and FITC dyed silica



SIMULATION

K. Stratford *et al.* *Science* **309**, 2198 (2005)



EXPERIMENT

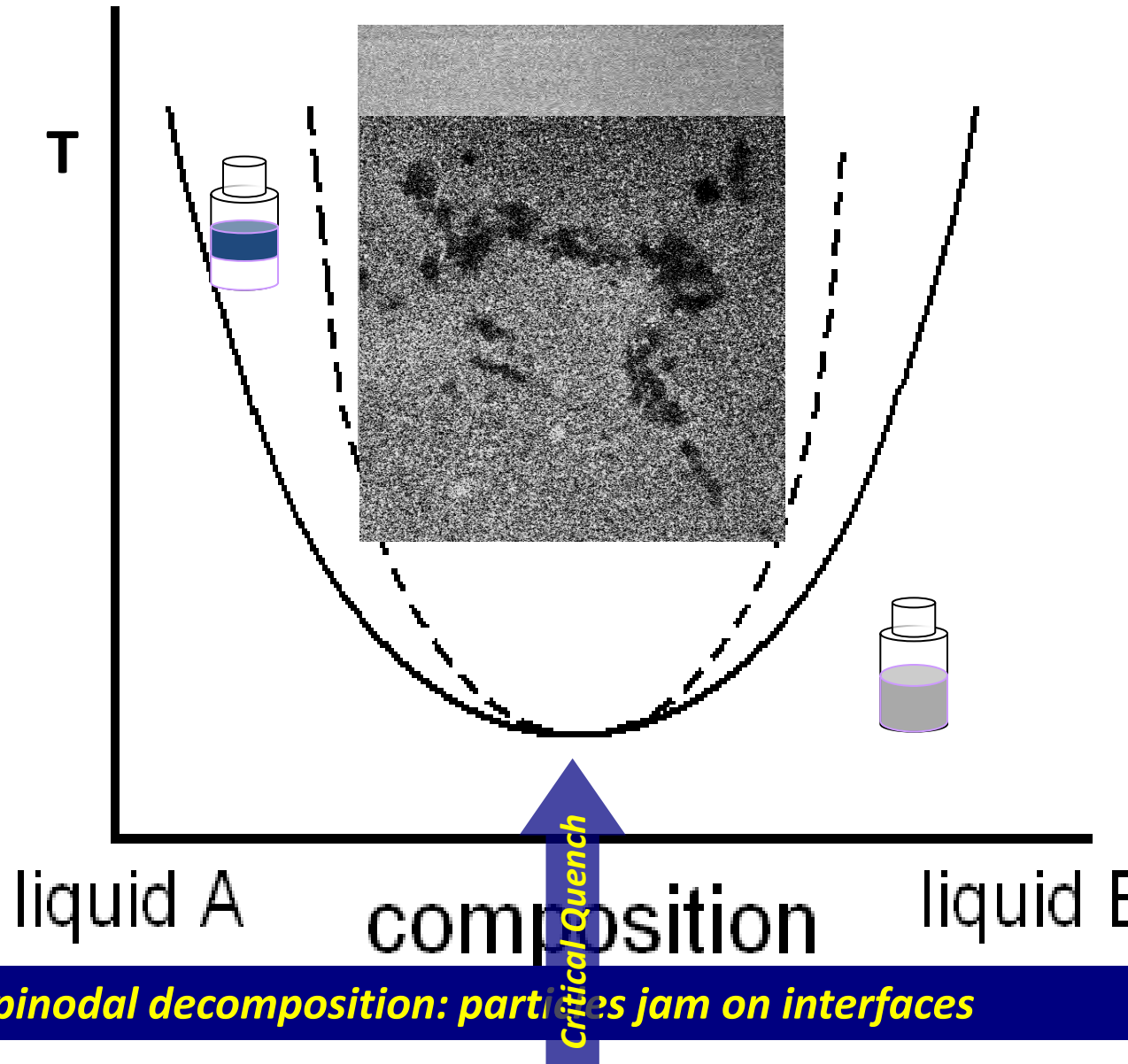
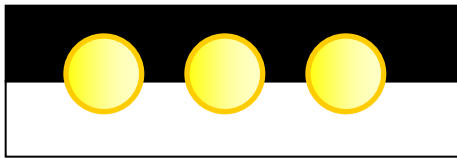
Herzig *et al* *Nature Materials* **6**, 966 (2007)

Bijel Fabrication

1) Partially miscible liquids

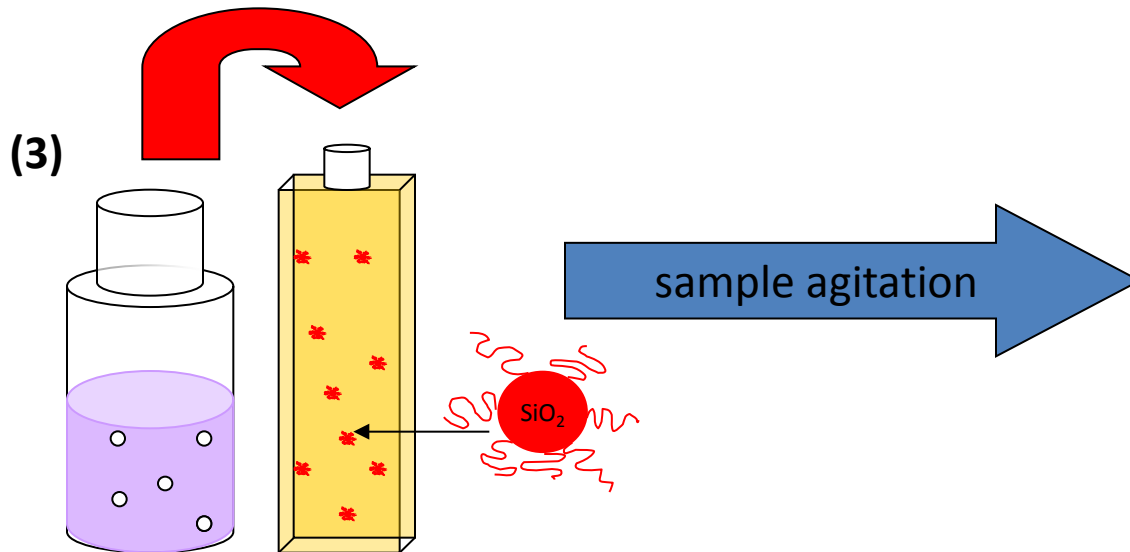
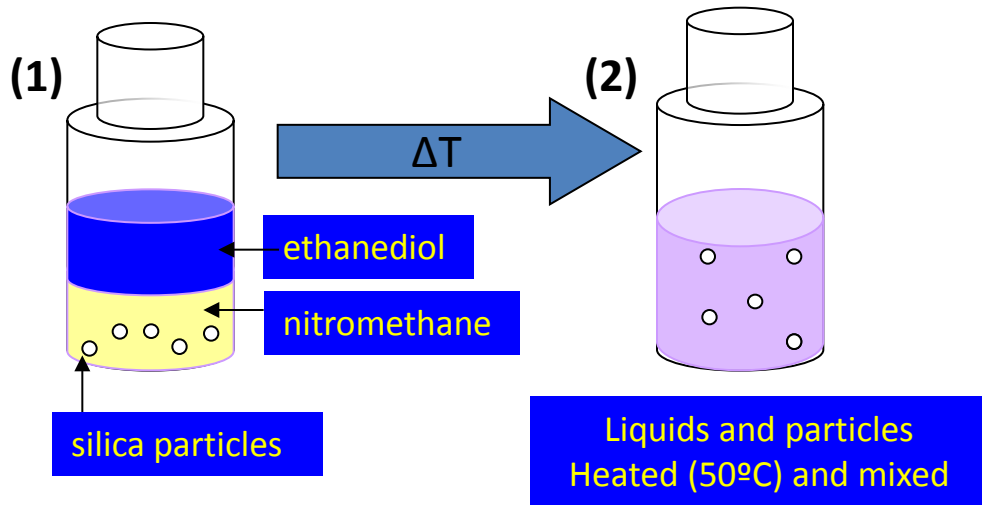
2) A critical composition

3) Neutrally wetting particles

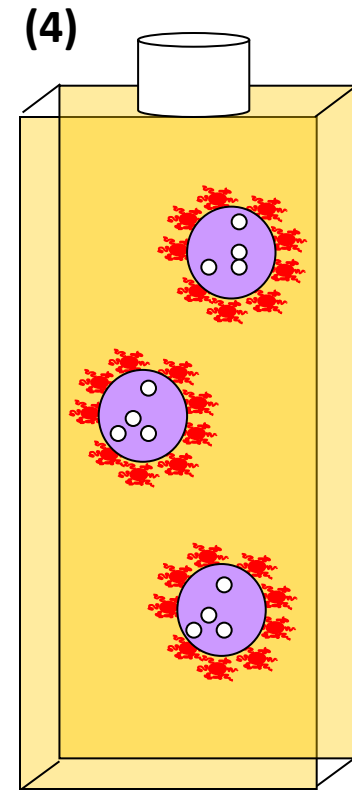


liquids separate via spinodal decomposition: particles jam on interfaces

Capsule fabrication



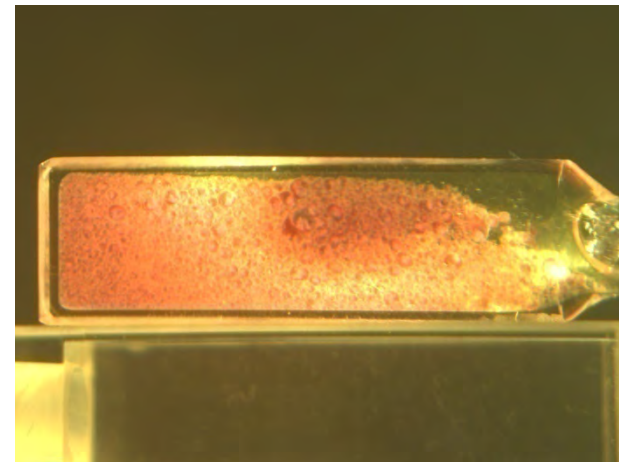
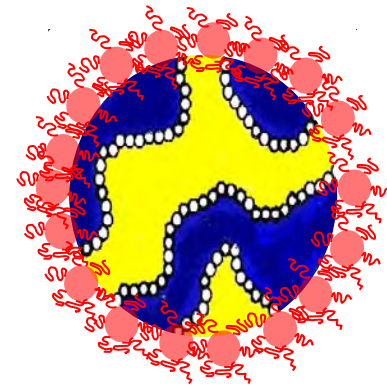
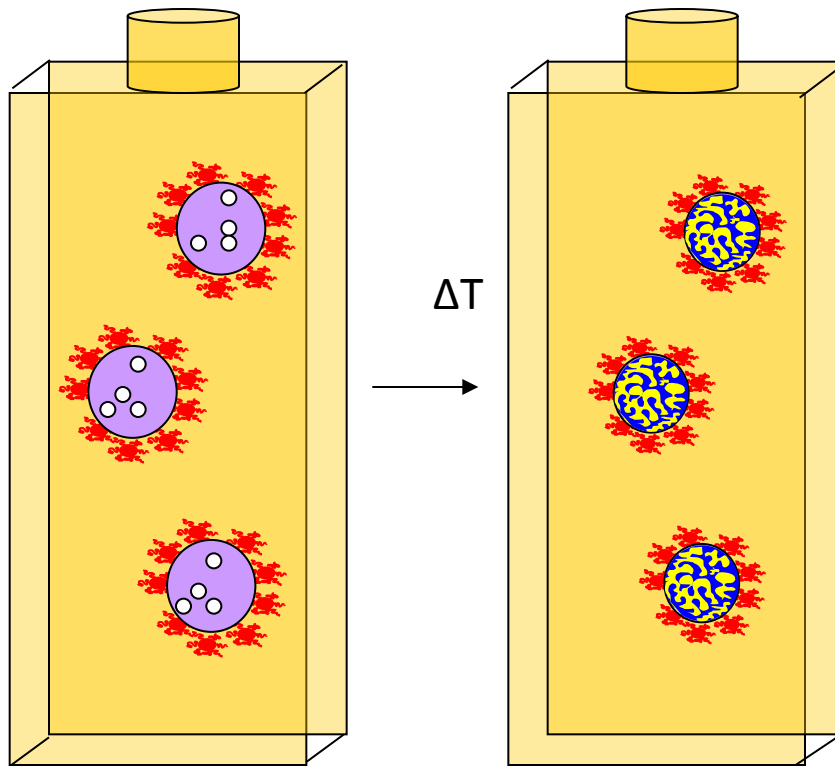
Still at 50°C mixture added to **dodecane** and **silica-g-poly-(12-hydroxystearic acid)** dispersion and agitated.....



A particle stabilised emulsion of the liquid mixture in dodecane

Capsule fabrication

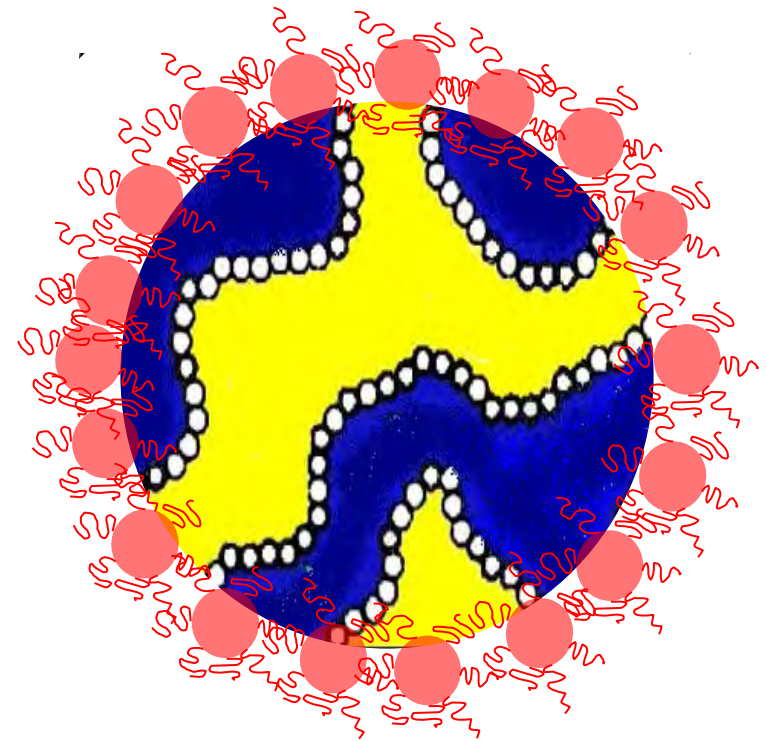
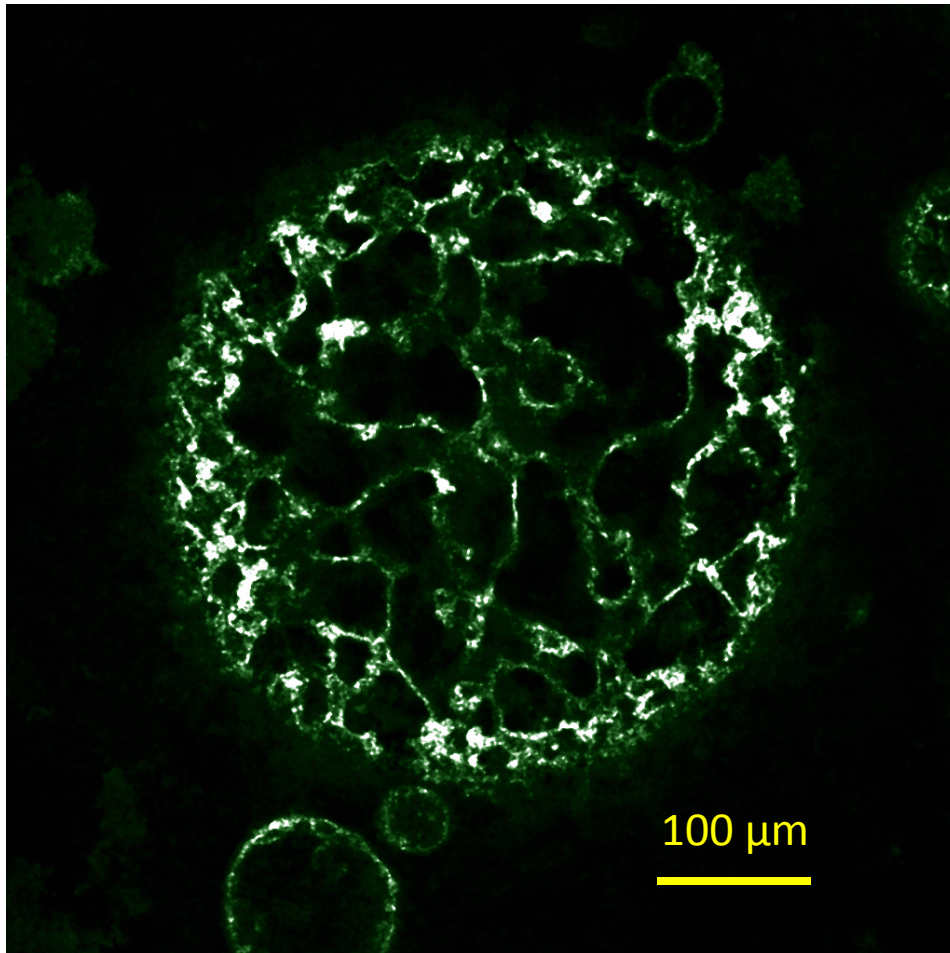
(4) continued



(5) Room temperature quench and bijel formation takes place in emulsion droplets forming the bijel capsule.

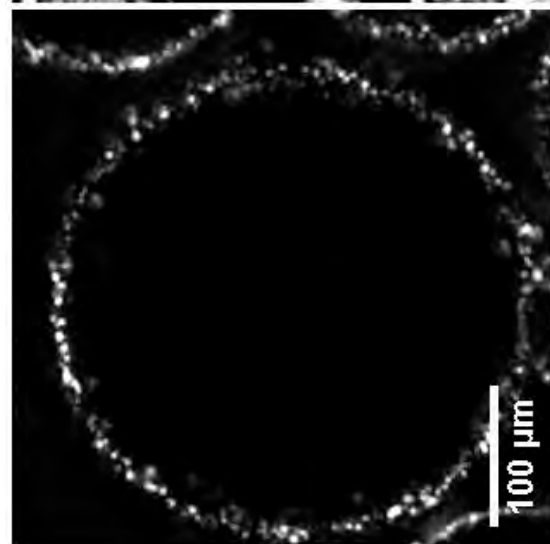
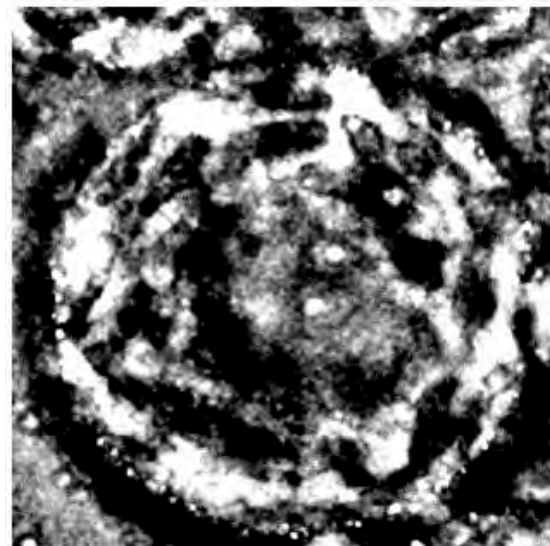
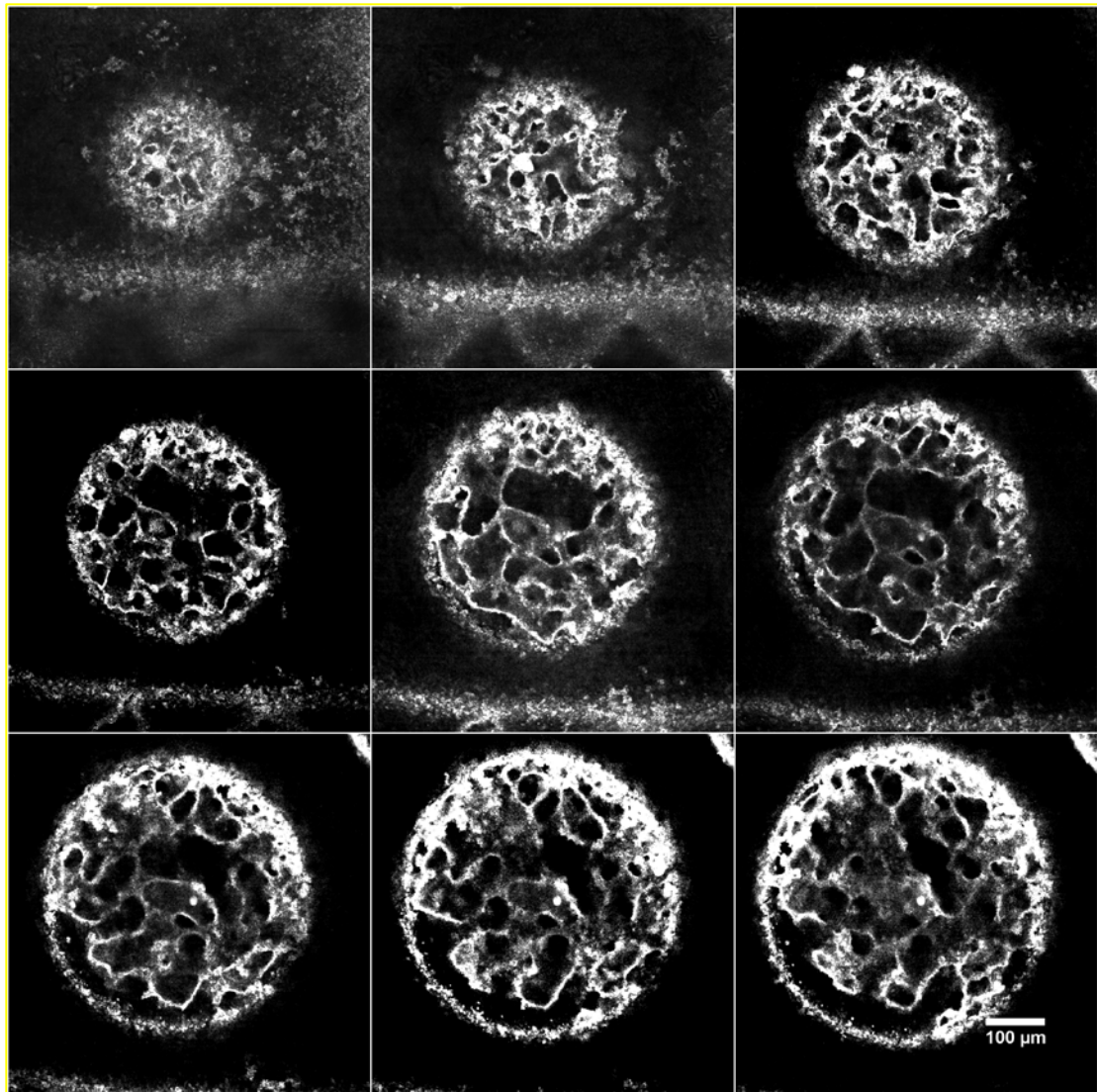
A Typical Bijel Capsule

Typical capsule size $> 100 \mu\text{m}$

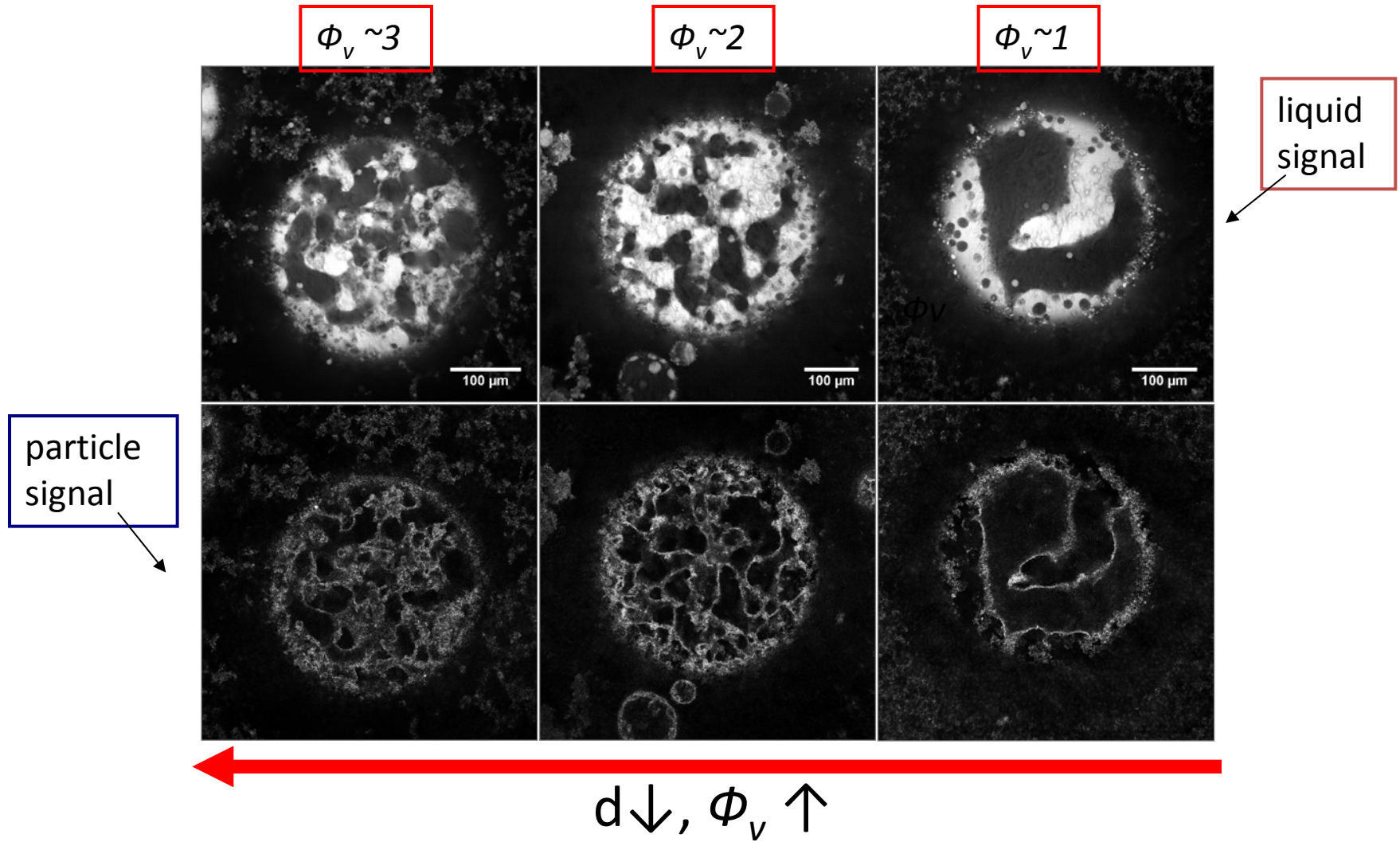


← Particle Signal

A More Detailed Look

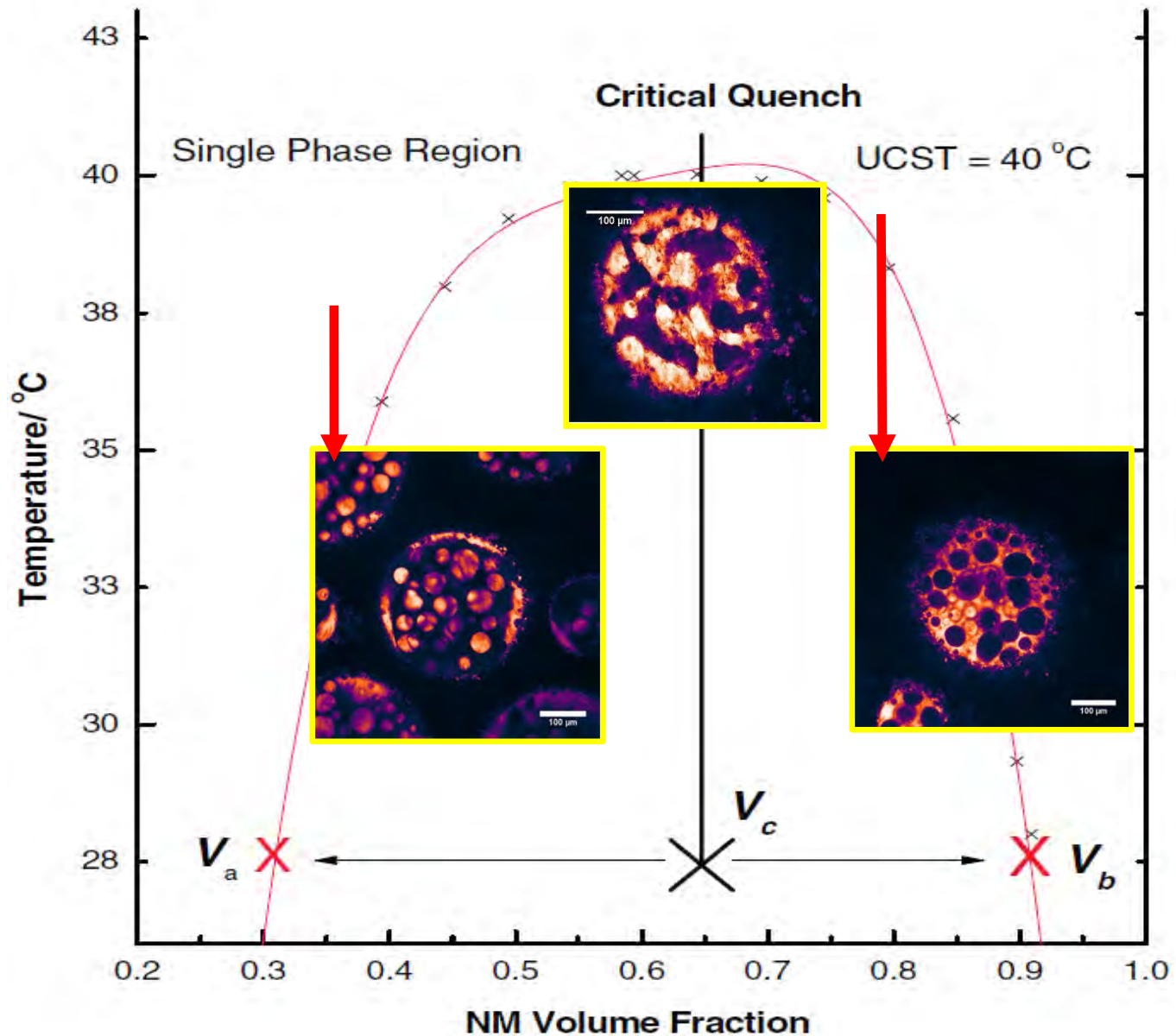


Manipulation of Architecture: Volume fraction

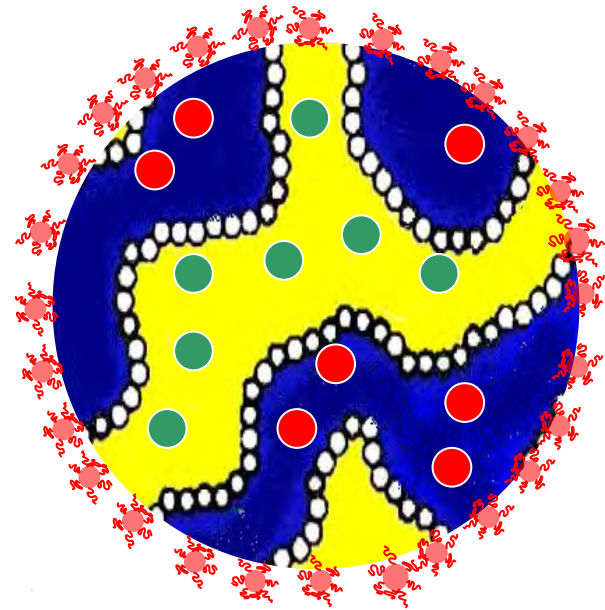
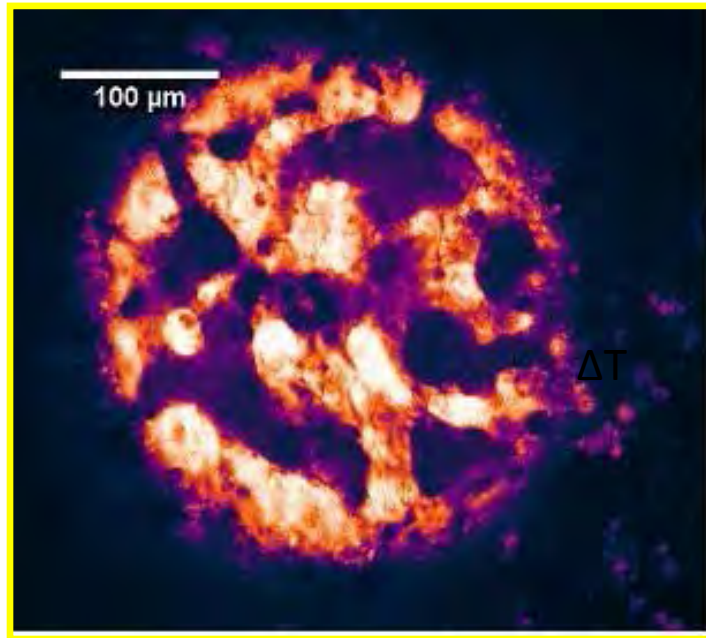


Qualitatively domain size, d , decreases with particle volume fraction, ϕ_v Area effect

Manipulation of architecture: Composition

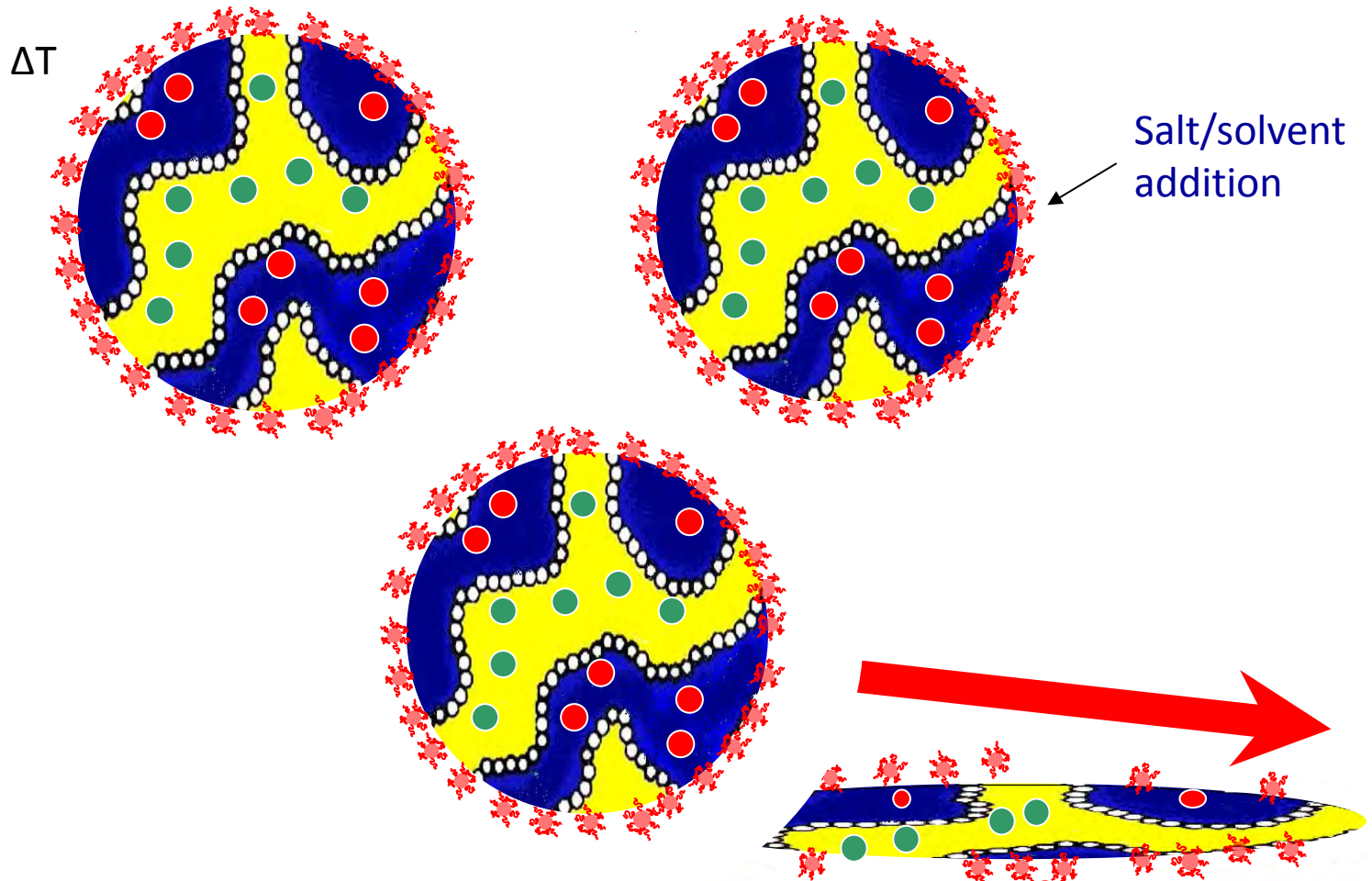


Encapsulation Advantages



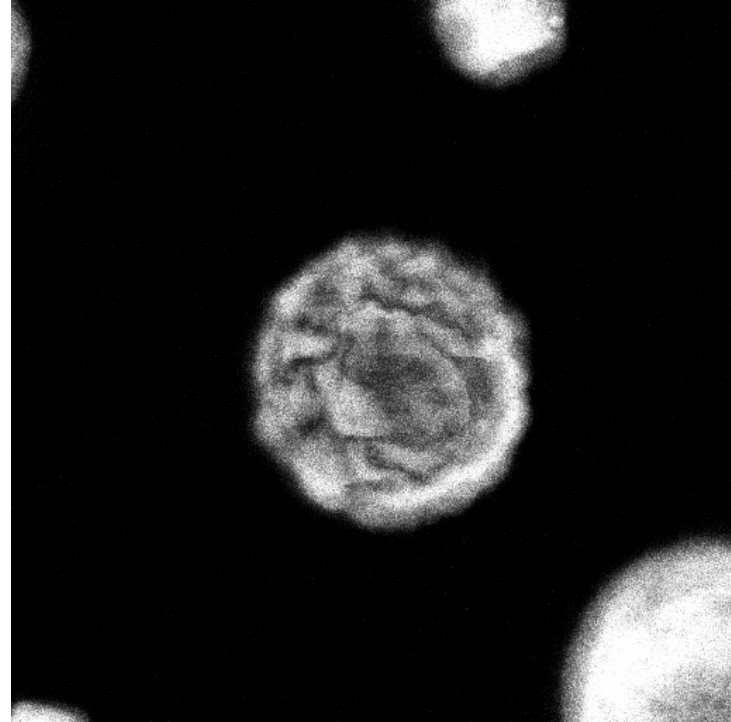
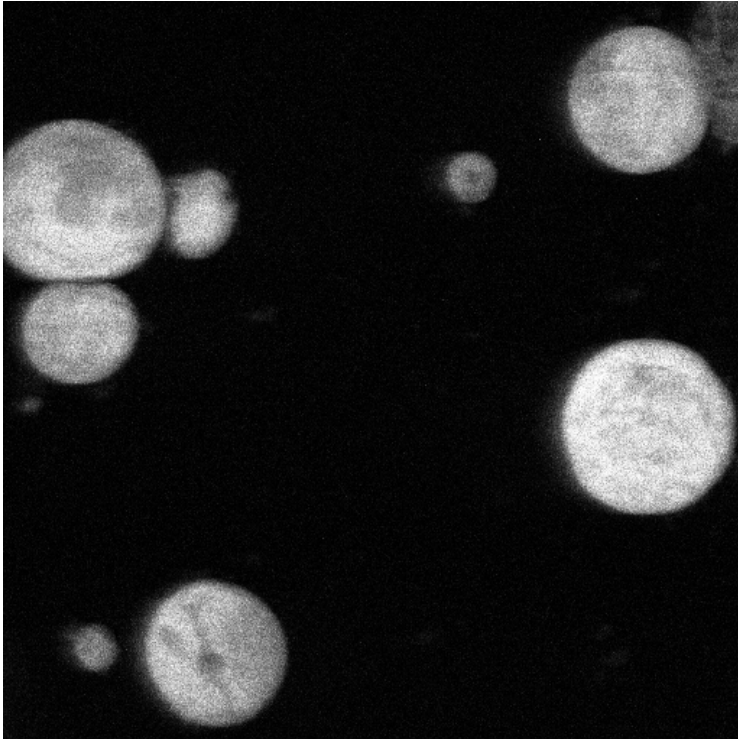
Can encapsulate 2 types of materials in equal amounts and release them in unison at equal rates.

Controlled Release: More Mechanisms

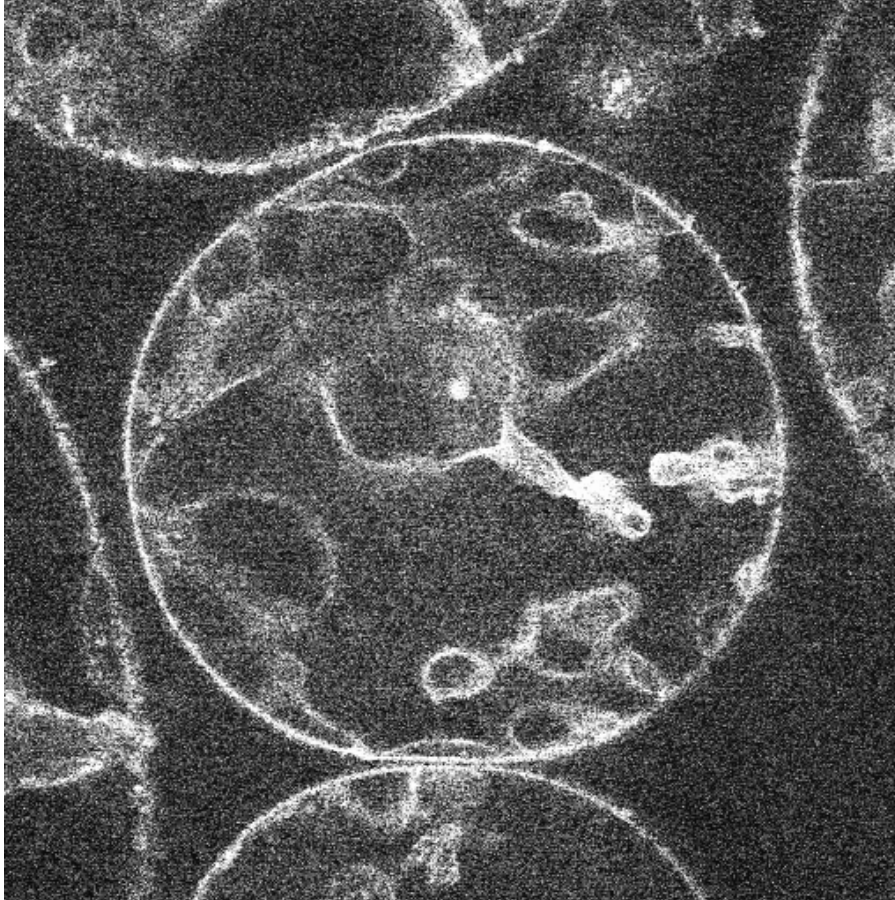


Encapsulation and controlled release is used in:
drug delivery, moisturisers, detergents, food flavouring

Triggered release(solvent induced)



T Response (Triggered Mixing)



On warming the capsule back into the single-fluid phase the liquids remix and the particles redisperse.

Useful for:

Keeping small particles inside?

*Environmentally responsive
Release (good for food flavours)*

Internal reactions?

Conclusions

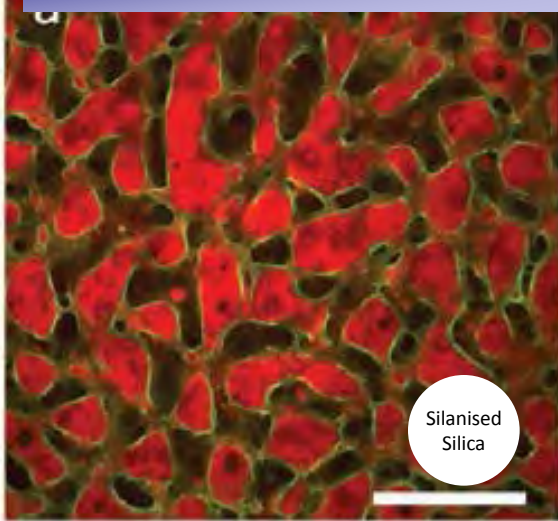
- We have demonstrated the generic route to form bijel capsules using ethanediol and nitromethane
- The ease with which domain size can be adjusted should allow control of release rates
- Bijel capsules allow, in principle, equal release rates of chemically distinct ingredients
- Trigger release/reaction
- Eliminate surfactants and polymers from emulsion system while keeping fluid phases continuous
- Dual function stabilizer (can be an active ingredient: TiO₂, ZAG)

THANKS FOR LISTENING!

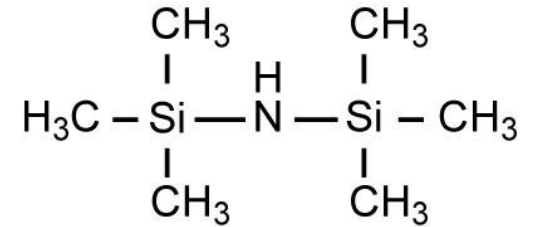


New Bijels

Cylohexene-Nitromethane

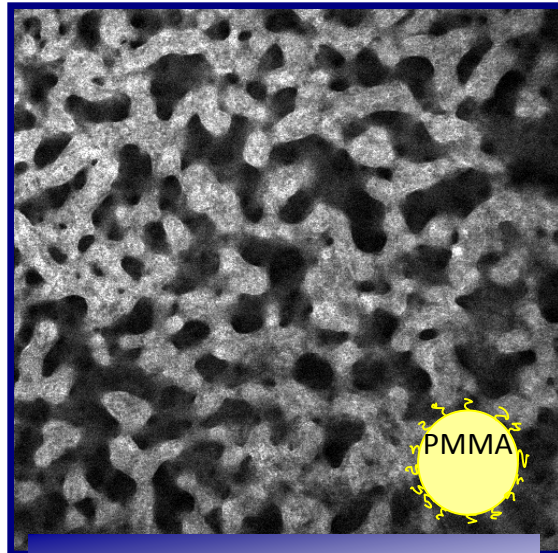
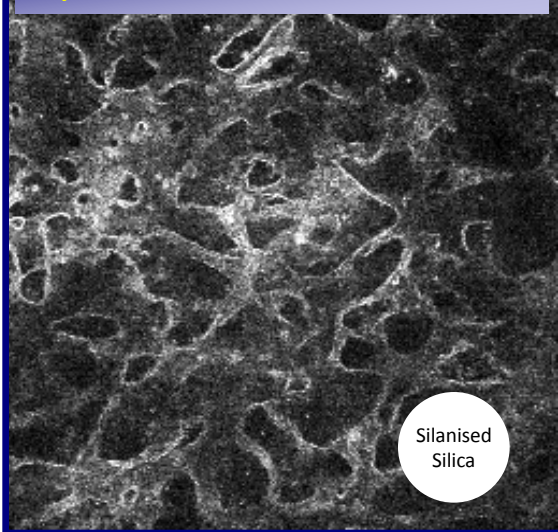


*Surface hydrophobicity of
Stöber silica tuned with HMDS:*

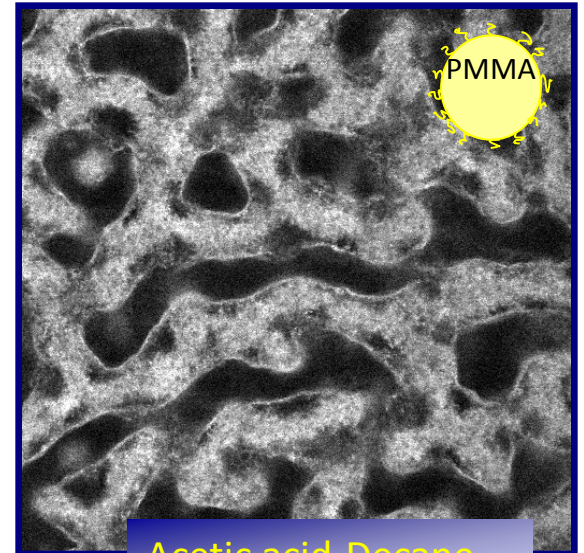


The Ethanediol-Nitromethane system is particularly stable.

Cylohexene-Nitromethane



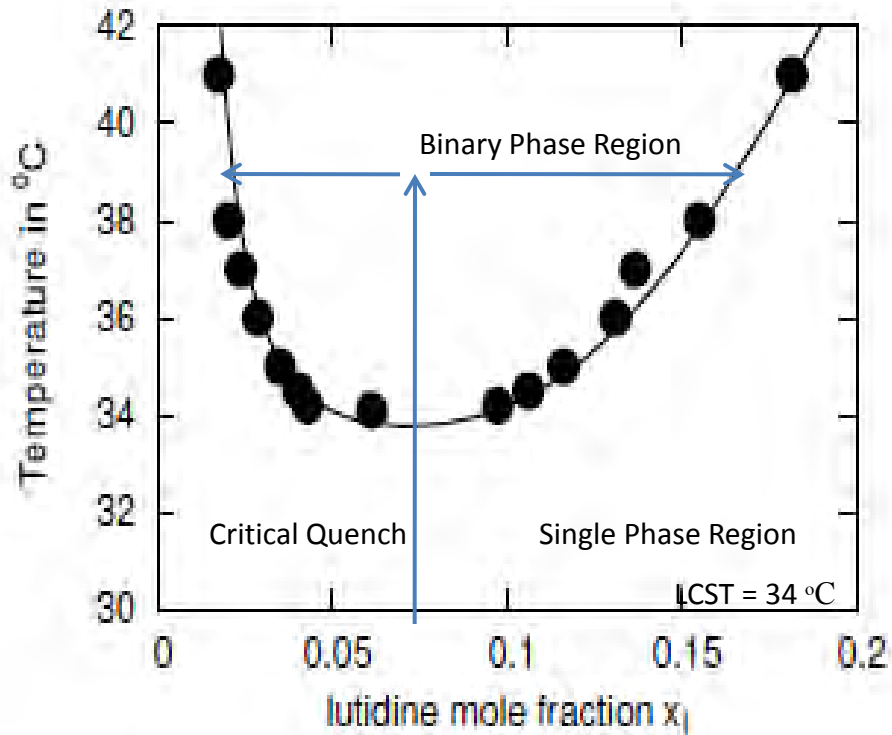
Ethanediol-Nitromethane



Acetic acid-Decane

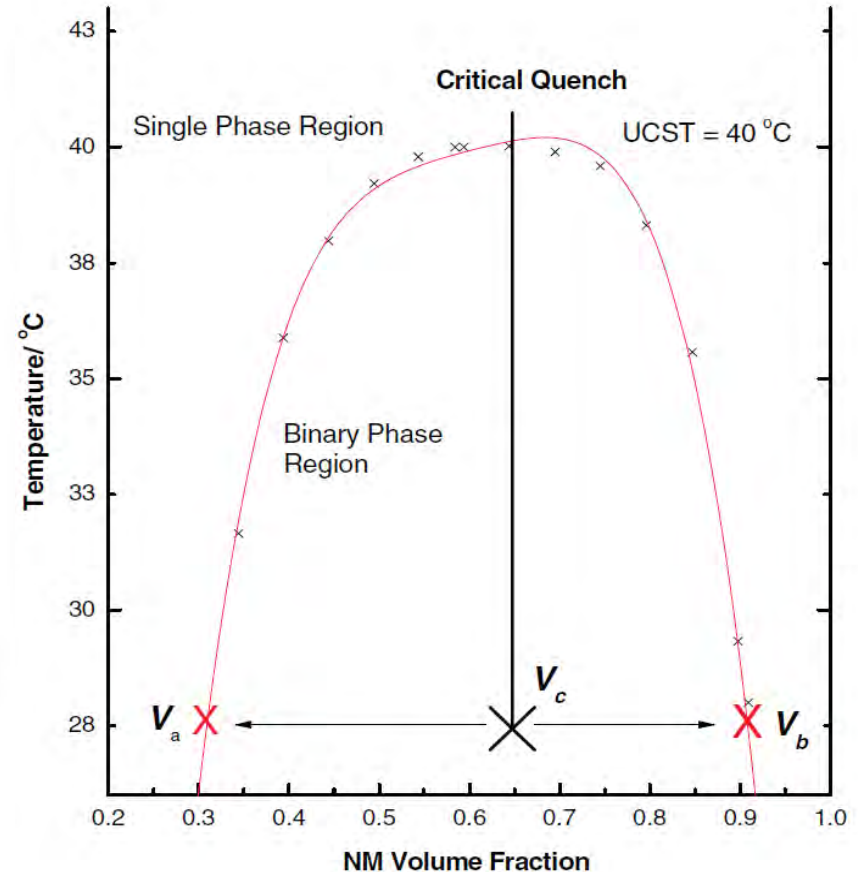
Why is the Nitromethan-Ethanediol System so Nice?

LUTIDINE - WATER



Density water = 1
 Density 2,6-lutidine = 0.925
 Volume Ratio: L:W - 38.9:61.1

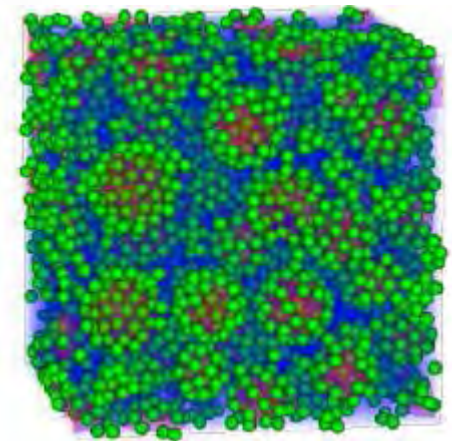
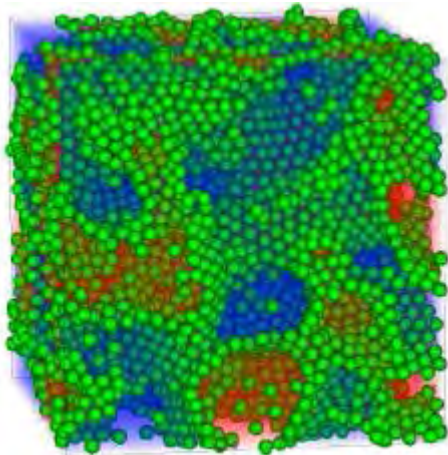
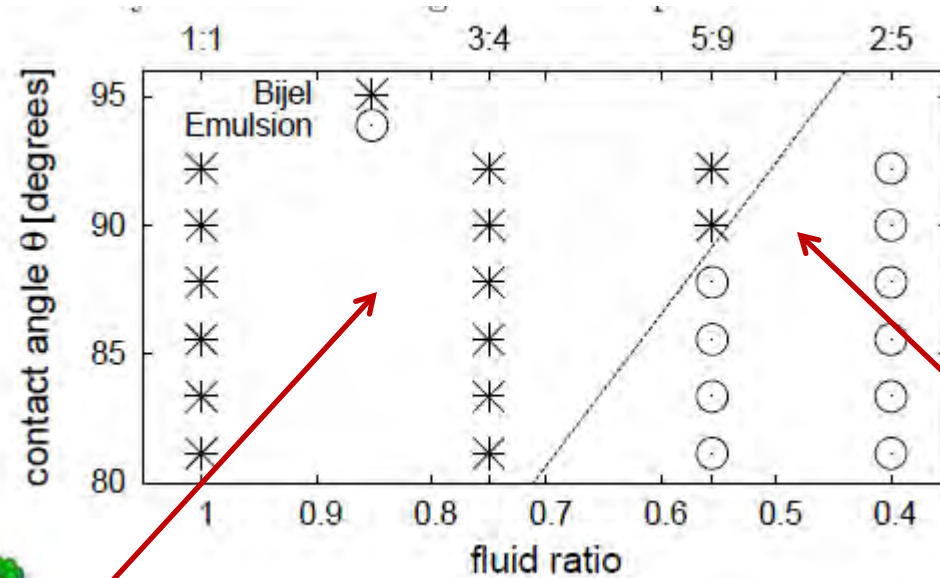
ETHANEDIOL - NITROMETHANE



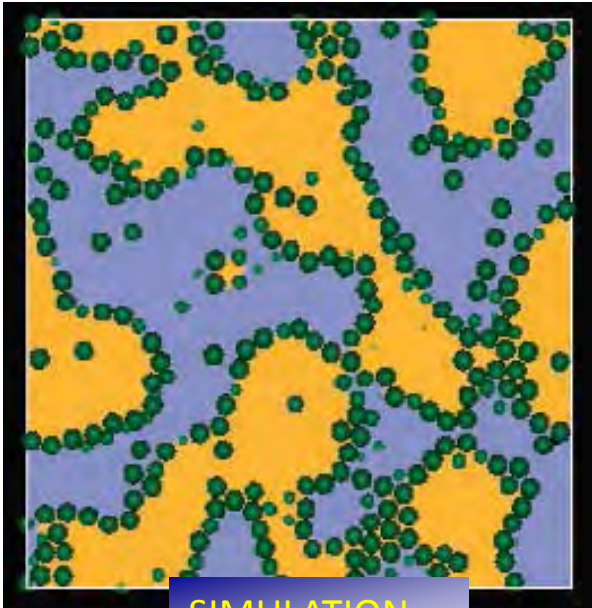
Density ethanediol = 1.1
 Density nitromethane = 1.1
 Volume Ratio: ED:NM - 48:52

Why is the Nitromethan-Ethenediol System so Nice?

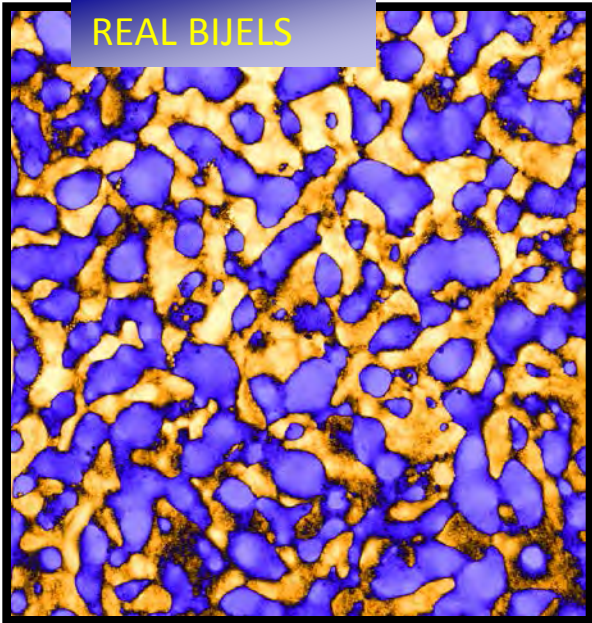
Equality of Volume



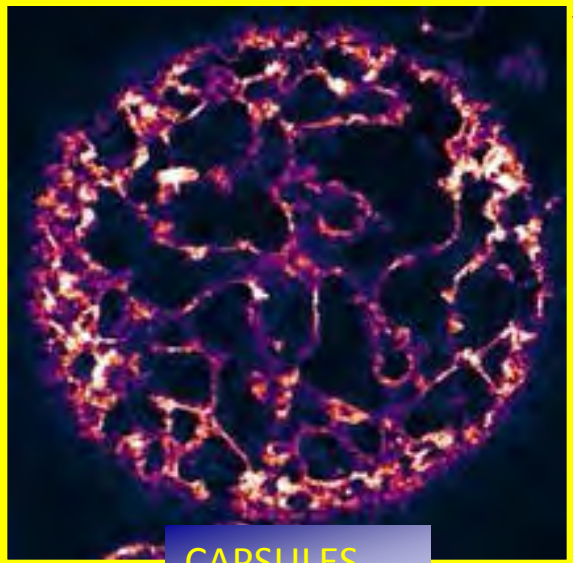
SUMMARY: BIJEL PROGRESSION



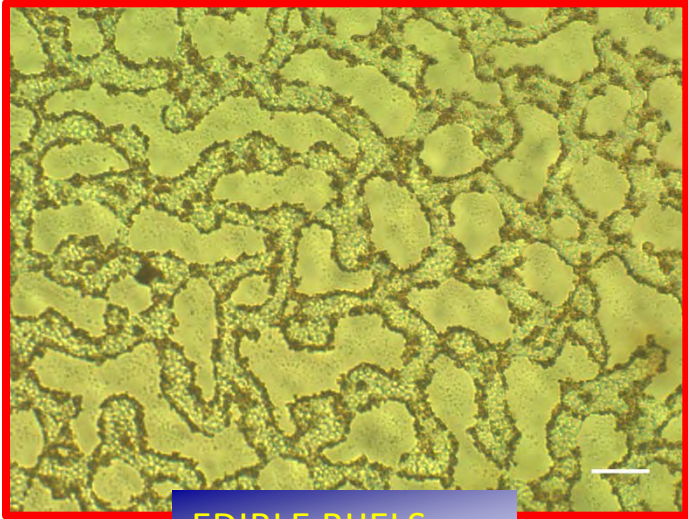
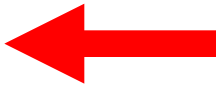
SIMULATION



REAL BIJELS

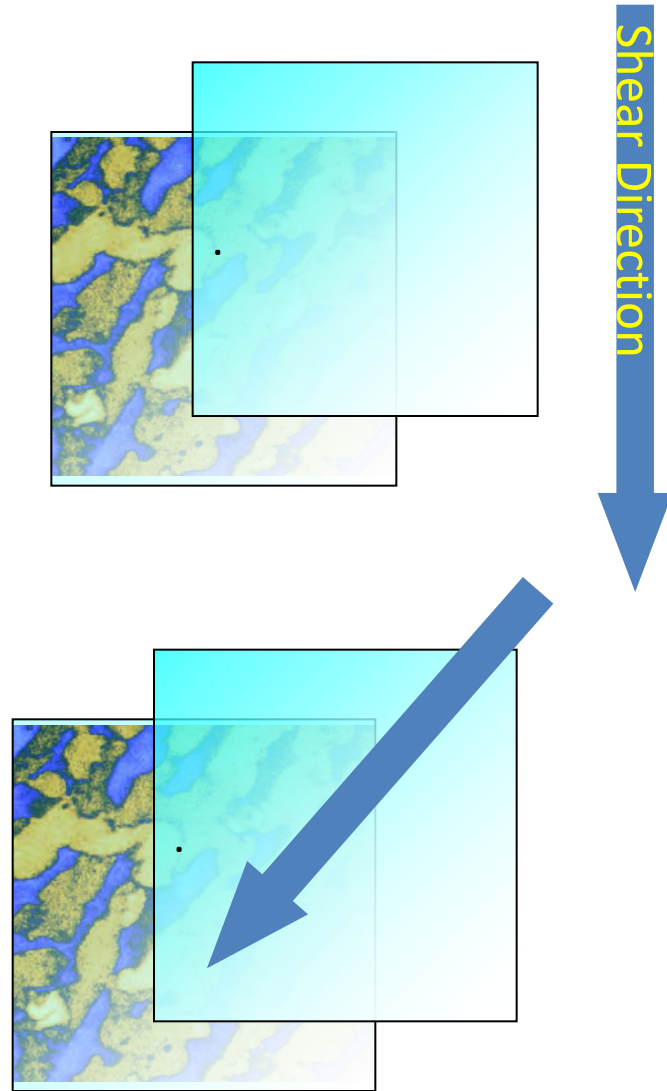
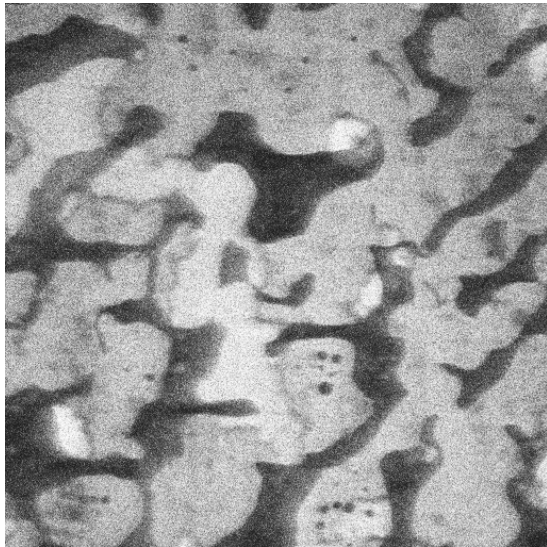
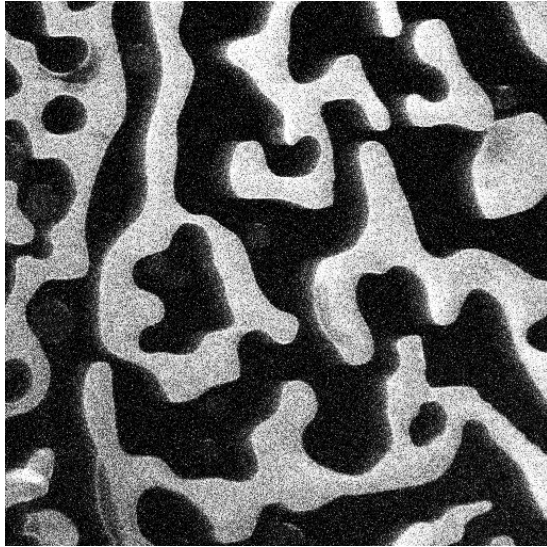


CAPSULES

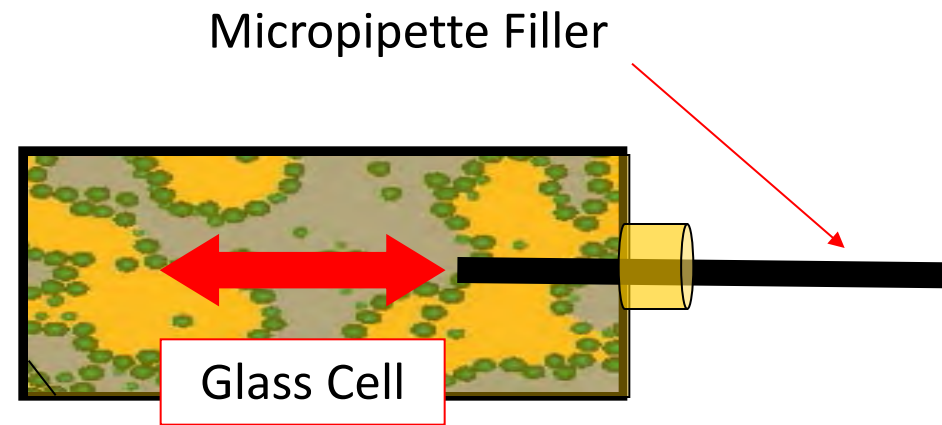
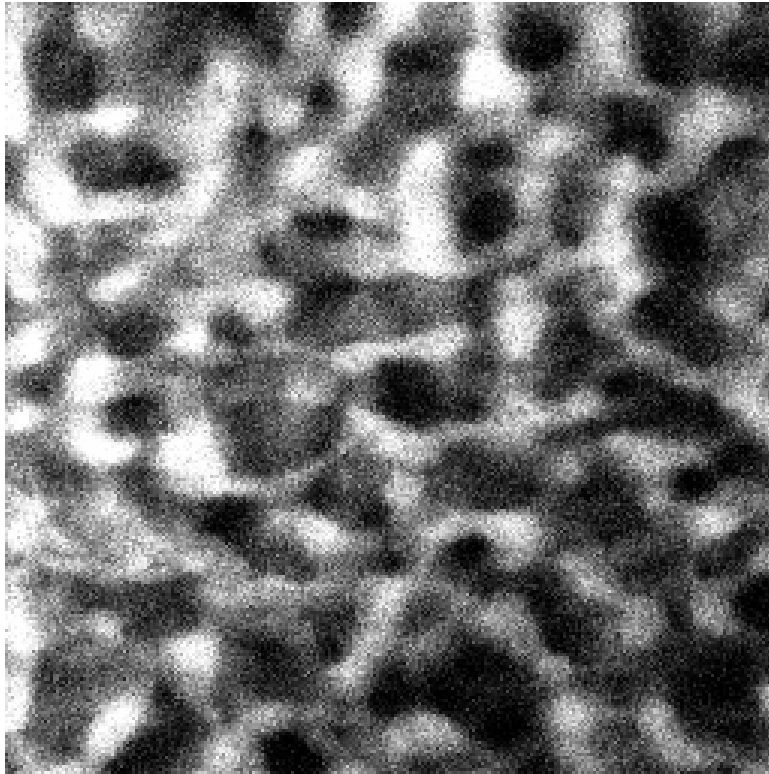


EDIBLE BIJELS

Response to shear



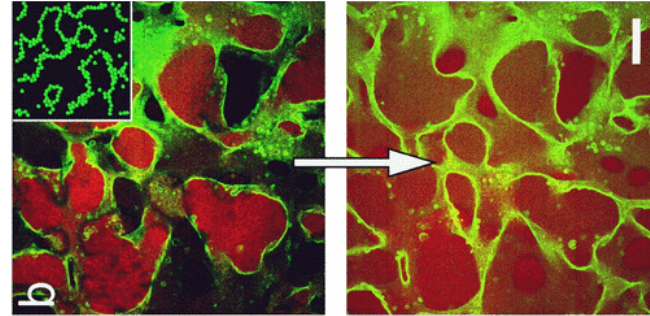
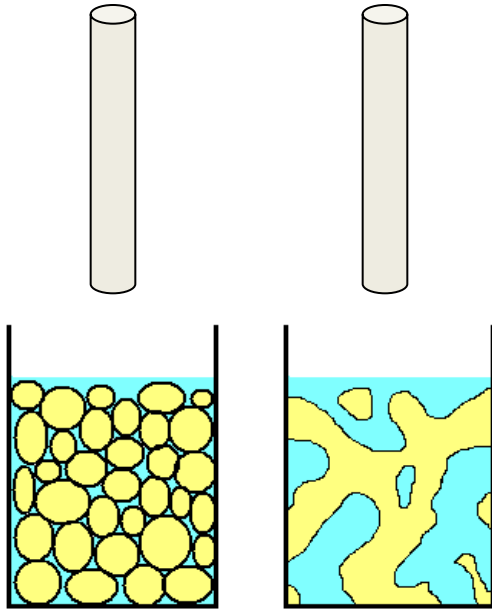
Response to compression



This basic experiment illustrates that the Bijel is elastic. The domains compress but after the removal of the micro syringe the Bijel returns to a near-original state.

Some Properties

(and possible applications)

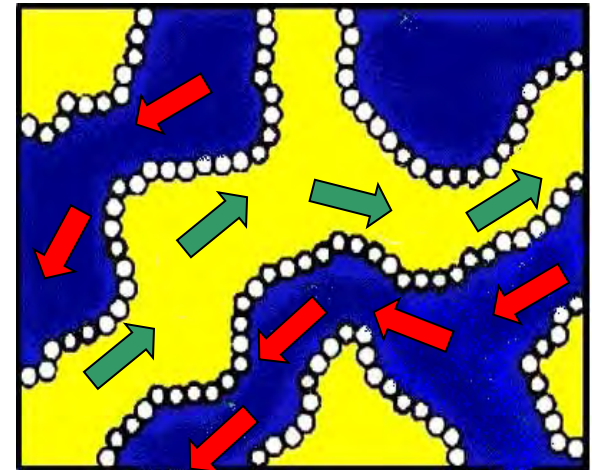
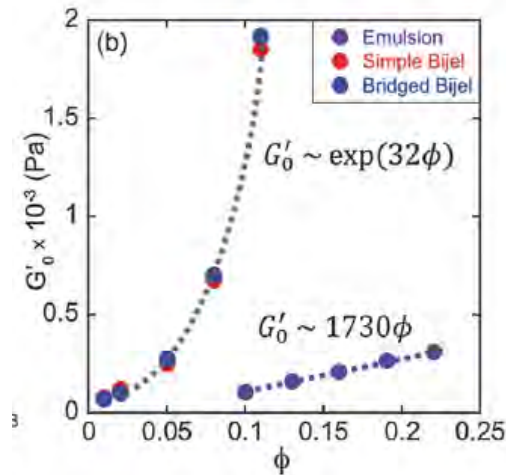


Capillary forces between particles

Sanz et al. *Phys. Rev. Lett.* **103**, 255502 2009



Viscoelastic



Flow and large surface area (purification of reactions, scaffold for tissue engineering)

Lower Bound Yield Stress = (cylinder weight) / (cylinder area) = 600 Pa