Controlling Product Microstructure

Pete Graham
Science Leader Processing of Microstructures
Unilever R&D Port Sunlight
Bebington, Wirral
peter.graham@unilever.com

Acknowledgements:
Carlos Gonzalez Lopez, Hazel Martin
& Joao Cabral Chemical Engineering,
Imperial College, London

Outline

1. Why does Product Microstructure matter?

2. How do structures form & some important factors

3. Batch mixers cf. short-residence time devices

4. Visualising structure formation and investigating its kinetics

5. Discussion

Unilever’s Brand Portfolio

Knorr
Dove
SUNSILK
Becel
Lipton
HELLMANN’S
dirt is good
Lifebuoy
CLEAR
LUX
Signal
Suave
AXE
Breyers
Vaseline
POND’S
Family Goodness
Surf
Rexona

Top 20 brands >70% of Unilever’s sales*

Microstructure & Product Properties

Consumers perceive differences in structured products:

visual appearance

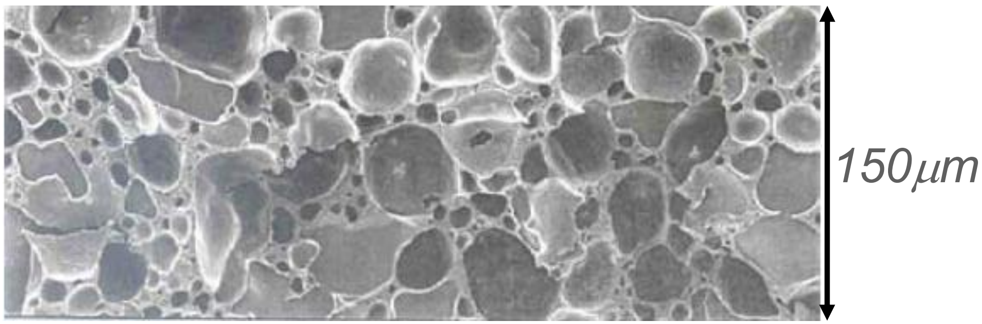
rheology & texture

dilution/dissolution

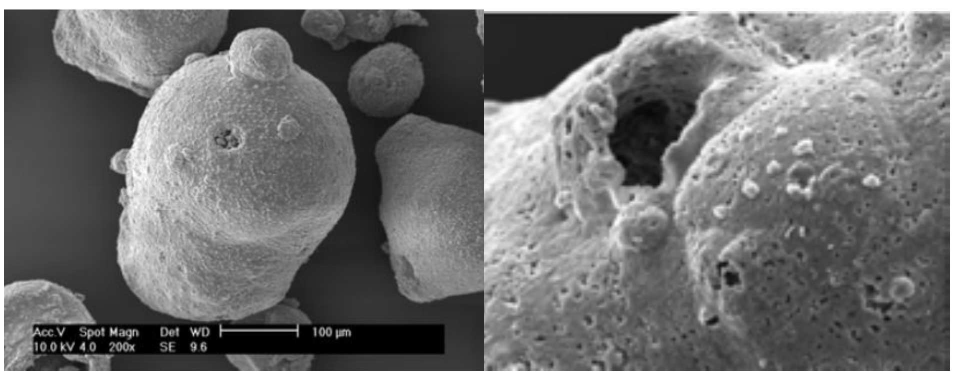
… and make their selection accordingly

Microstructure and Product Properties

a). The size of ice crystals and perception of creaminess in ice-cream …



b). The porosity of detergent powders and dissolution



a). Crilly et al, Ind & Eng Chem Res, 47, 6362-67 (2008)
b). B Carroll, J Dispersion Sci & Tech, 29, 1349-53 (2008)

Microstructure and Liquids Processing

Dominant factors:

- Phase Behaviour
  - temperature
  - concentration
  - flow
- Colloidal Interactions

Final product properties depend on the pathway through a series of transient conditions

Polymer Structuring

Polymer or biopolymer structuring:

- Toothpastes
- Shampoo/Body Wash liquids
- Ready-made Bouillons
- Sauces and Salad Dressings

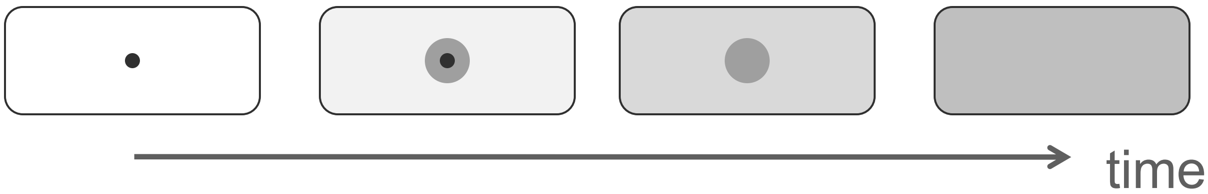
The polymers provide:

- particle/droplet suspension, deposition
- preferred rheological profiles and textures

However, there is only limited understanding of the mechanisms of structure formation, during and immediately after manufacture

D Franzo et al, J Dentistry, ***38****, 974-79 (2010)*
S Roller & ICM Dea, Critical Reviews in Biotechnology, **12**, 261-277 (1992)
MA Brown et al, International Journal of Cosmetic Science, ***32****, 193–203 (2010)*

Polymer Particle Dissolution



What are the overall kinetics?

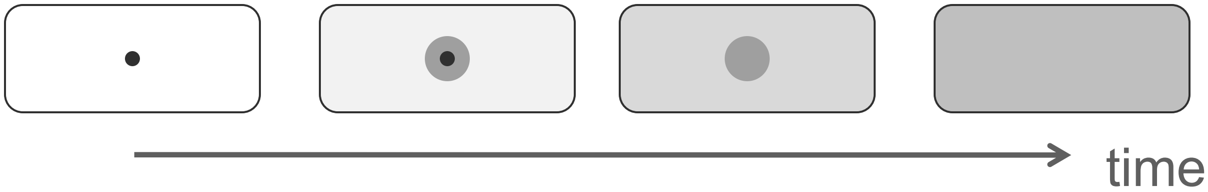
What is the mechanism?

When polymer particles are no longer visible is the process complete?

How much further equilibration is involved to establish a ‘final’ conformation?

How does that change within storage conditions?

Polymer Particle Dissolution - 2

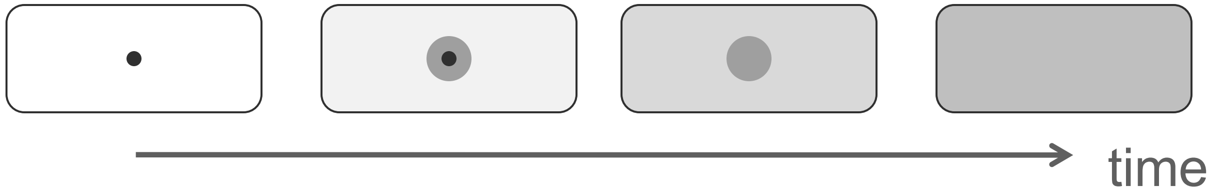


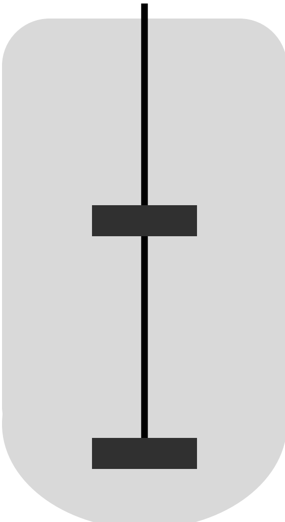
What happens when other ingredients are added?

salt solutions
non-solvents
solid particles

Evidently these system interactions are complex

Polymer Structuring



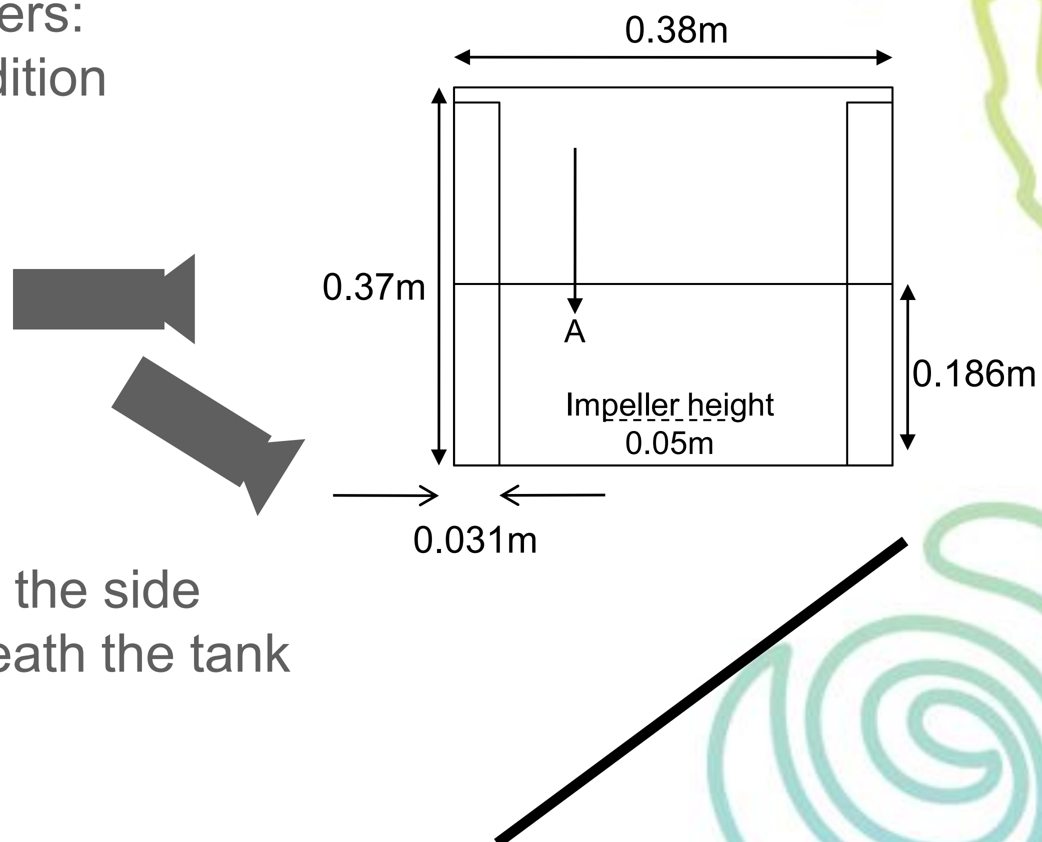


The complexity is exaggerated by variation in local concentration conditions within batch mixers

Extent of dissolution becomes a function of location within the vessel?

Flow Visualisation in Baffled Stirred Tank

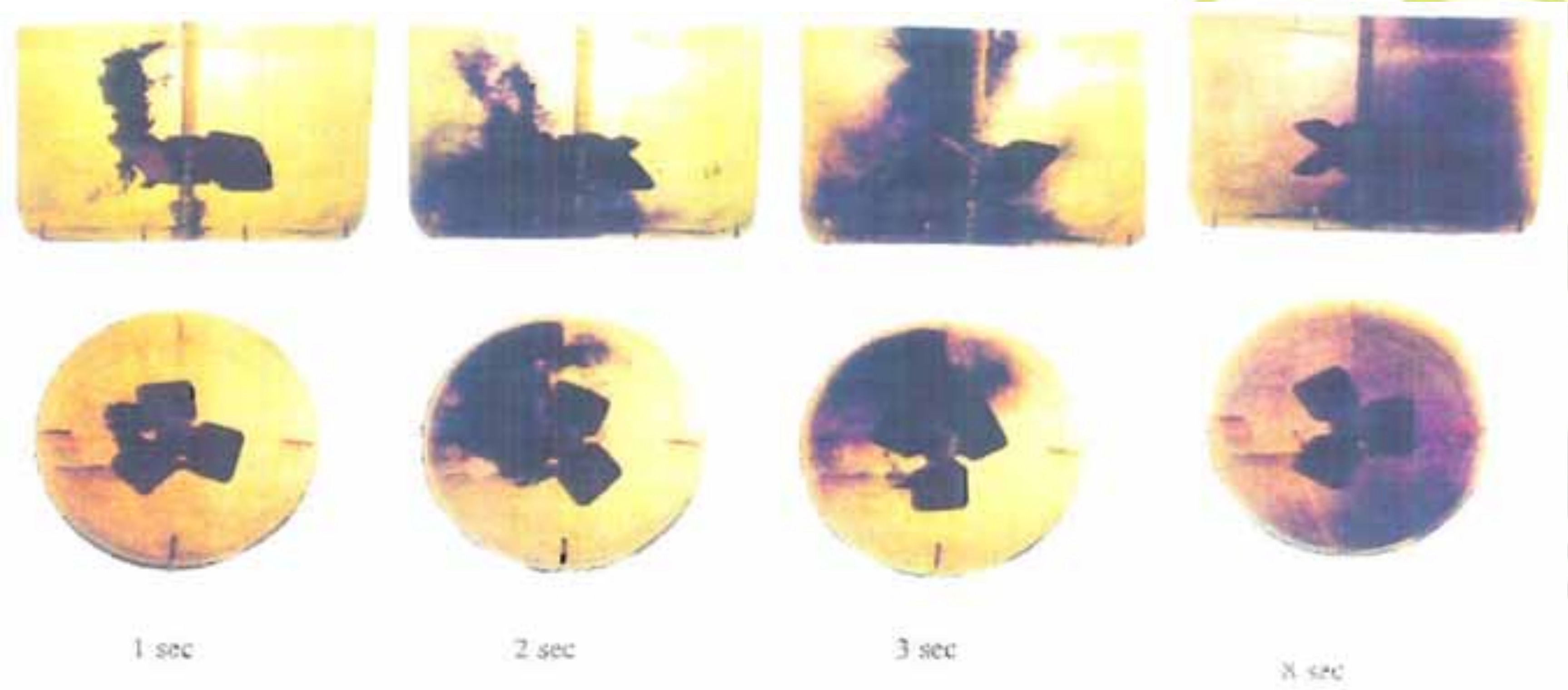
Comparison of turbine and axial flow impellers: with sub-surface addition of dye to water



Video recorded from the side and on a mirror beneath the tank

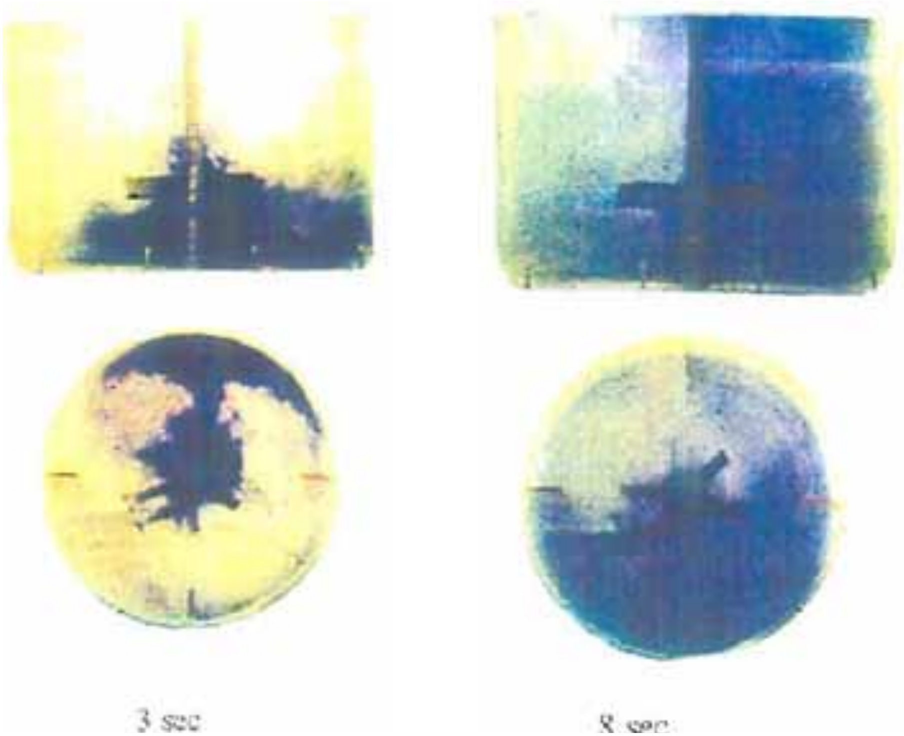
Graham, Edwards, Mann, Togatorop AIChE Conference (1995)

Flow Visualisation in Baffled Stirred Tank



Wide variations in concentration, over extended periods

Flow Visualisation in Baffled Stirred Tank



Wide variations in concentration, over extended periods

Reproducibility depends on precise addition points, geometry, fill/addition rates & ratios, agitator/baffle designs *etc*

Flow Visualisation in Baffled Stirred Tanks

A range of techniques to visualise this complexity: *PIV, CFD etc*

- flow
- concentration

Challenging in reactive systems

$$A + 2B \rightleftharpoons C$$

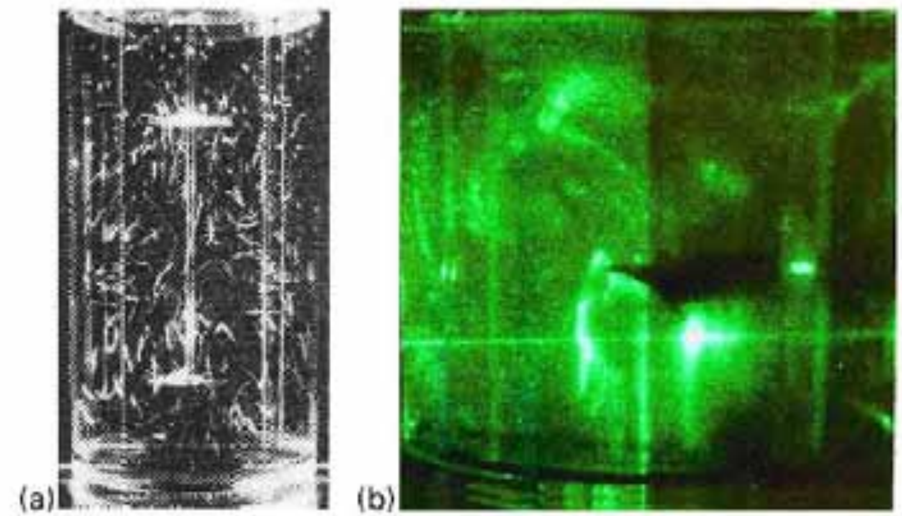


Figure 8. Streak-line identification of principal flow patterns in stirred vessels: (a) tall (H = 2T) vessel with two HE-3 impellers[9]; (b) stirred vessel with a single Mixel TT impeller [P. Mavros, unpublished work].

Very challenging in systems with non-stoichiometric reactions & physical interactions

Mavros, Trans IChemE, Vol 79A, pp 113-127 (2001)

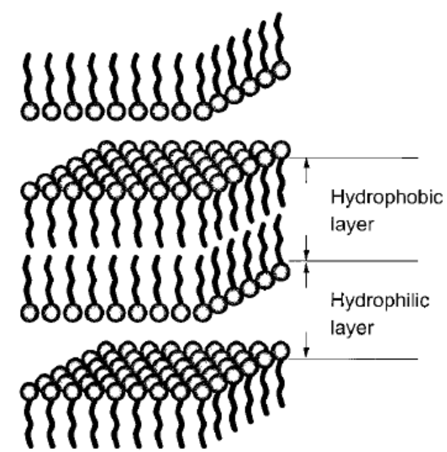
Liquid Crystal Dispersions

Many surfactants readily
form liquid crystal dispersions
in water:

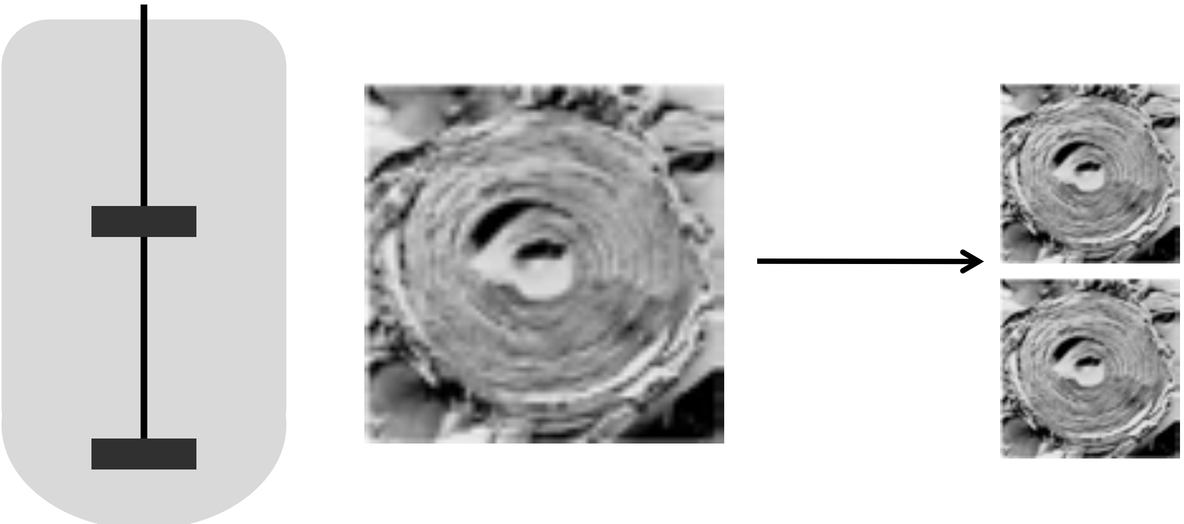
Lamellar Dispersions

- Hair & Fabric Conditioners
- Liquid Abrasive Cleaners
- Skin Creams

Lamellar morphologies include
bundles of parallel bilayer sheets
& multi-lamellar vesicles



Liquid Crystal Dispersions



Break up can occur under shear & extensional forces – vesicles comparable with lengthscales of mixing

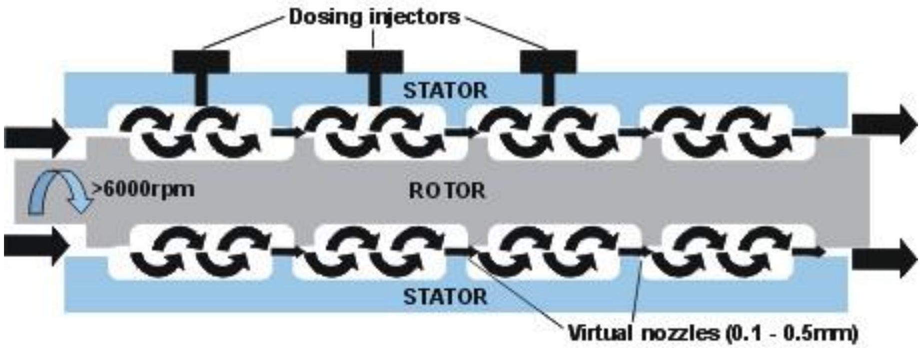
Kolmogorov – eddy lengthscale $\alpha\ (\upsilon^3 / \varepsilon)^{1/4}$

Where υ = kinematic viscosity and ε = energy dissipation rate

Residence times in regions of specific energy dissipation?

K Mortensen, Current Opinion in Colloid & Interface Science, **6**, 140-45 (2001)
Landahl & Mollo-Christensen, Turbulence and Random Processes in Fluid Mechanics. Camb, 2ed, 1992

Short-Residence Mixing Devices



Controlled Deformation Dynamic Mixer (Maelstrom)

Nozzle-Blade Mixers (Sonic)

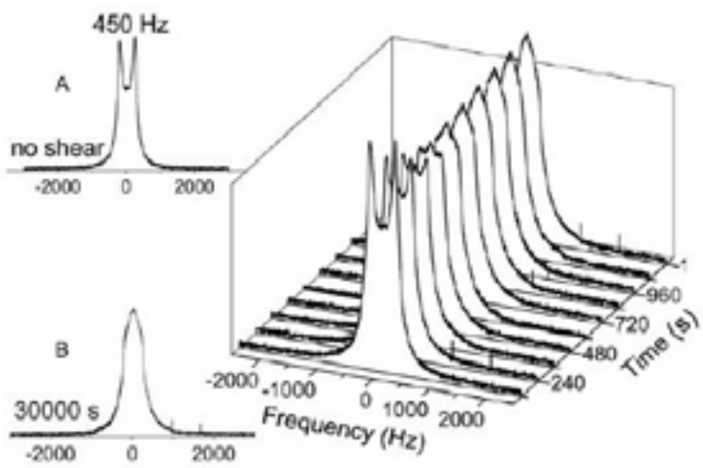
Screen Rotor-Stator Mixers (Silverson)

All can provide residence times <1s
- much more tightly defined flow conditions
- material exposed to consistent field

BUT WHAT ARE THE KINETICS?

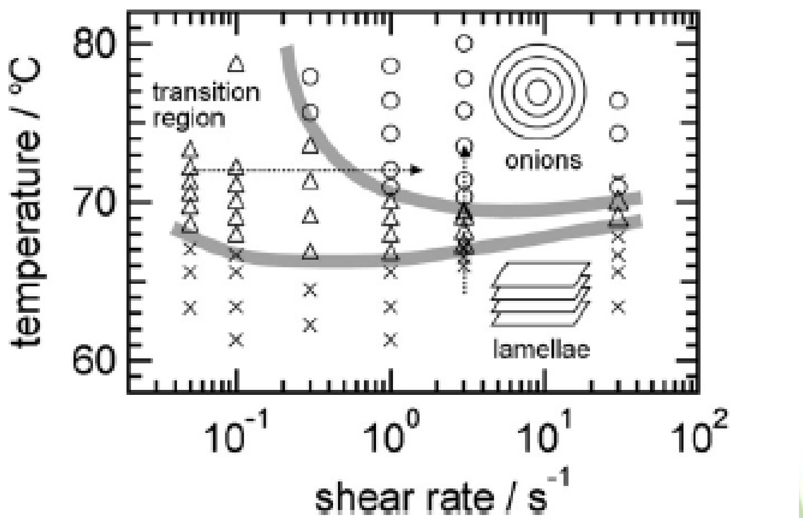
Liquid Crystal Dispersions

a).



^{1}H evidence of lamellar to vesicle transition in $C_{16}E4$ nonionic surfactant at 40'C due to constant shear-rate ($0.5s^{-1}$) for upto 30,000s

b).

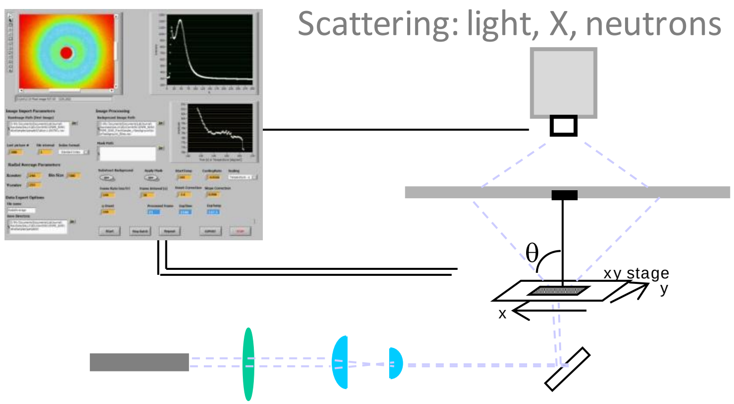


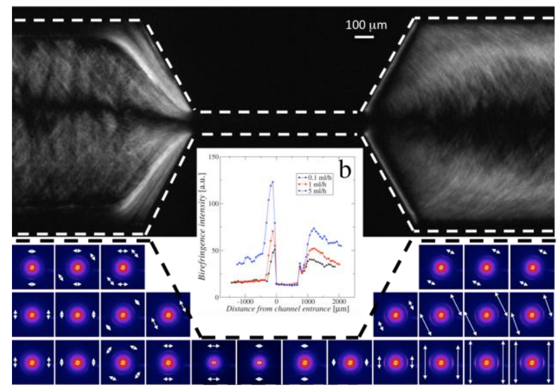
Temp vs shear-rate diagram for $C_{16}E7$ in D_2O, based on Rheo-SAXS experiments

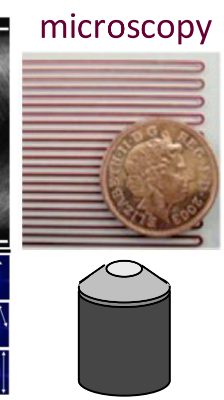
(a) L Gentile et al, J Coll & Interfac Sci, 362, p1-4 (2011)
(b) M Ito et al, Langmuir, 27, 7400-7409 (2011)

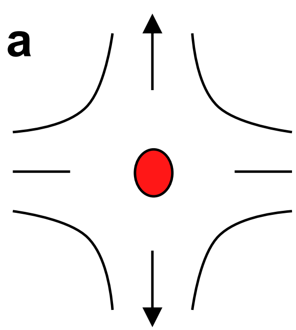
Visualise Mechanisms & Kinetics

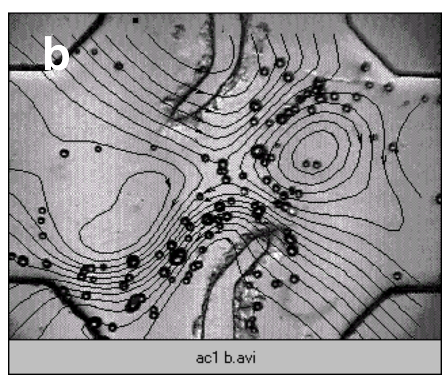
Use microfluidic devices to investigate structure formation

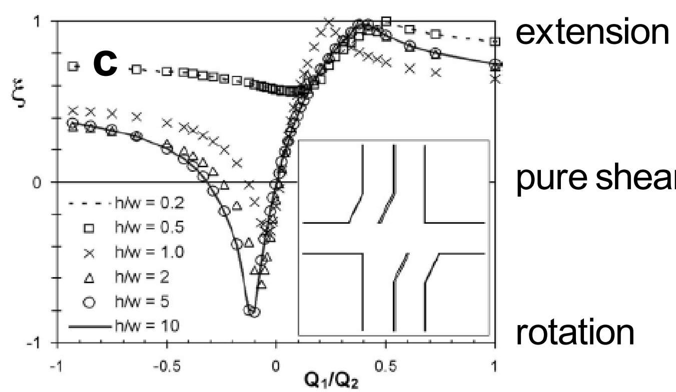




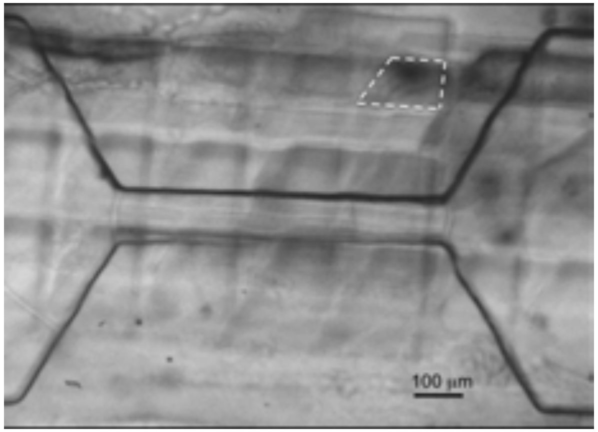




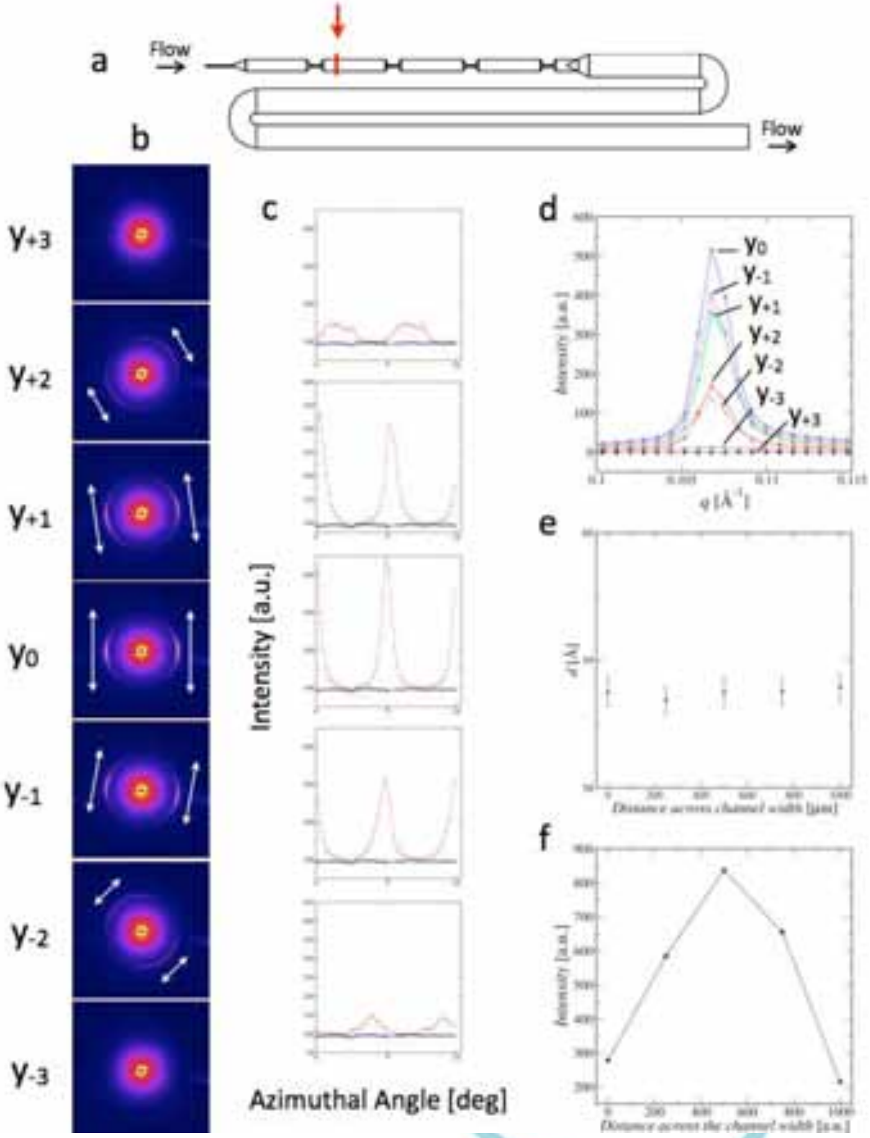




Liquid Crystal Dispersions



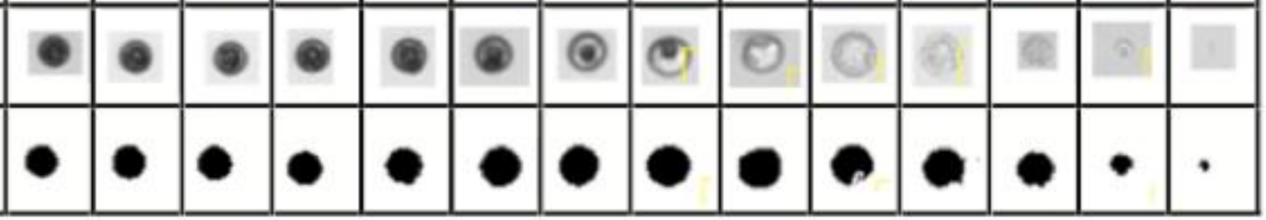
Direct observation of vesicle rotation and alignment of the lamellae with/against the flow depending on their position within the channel

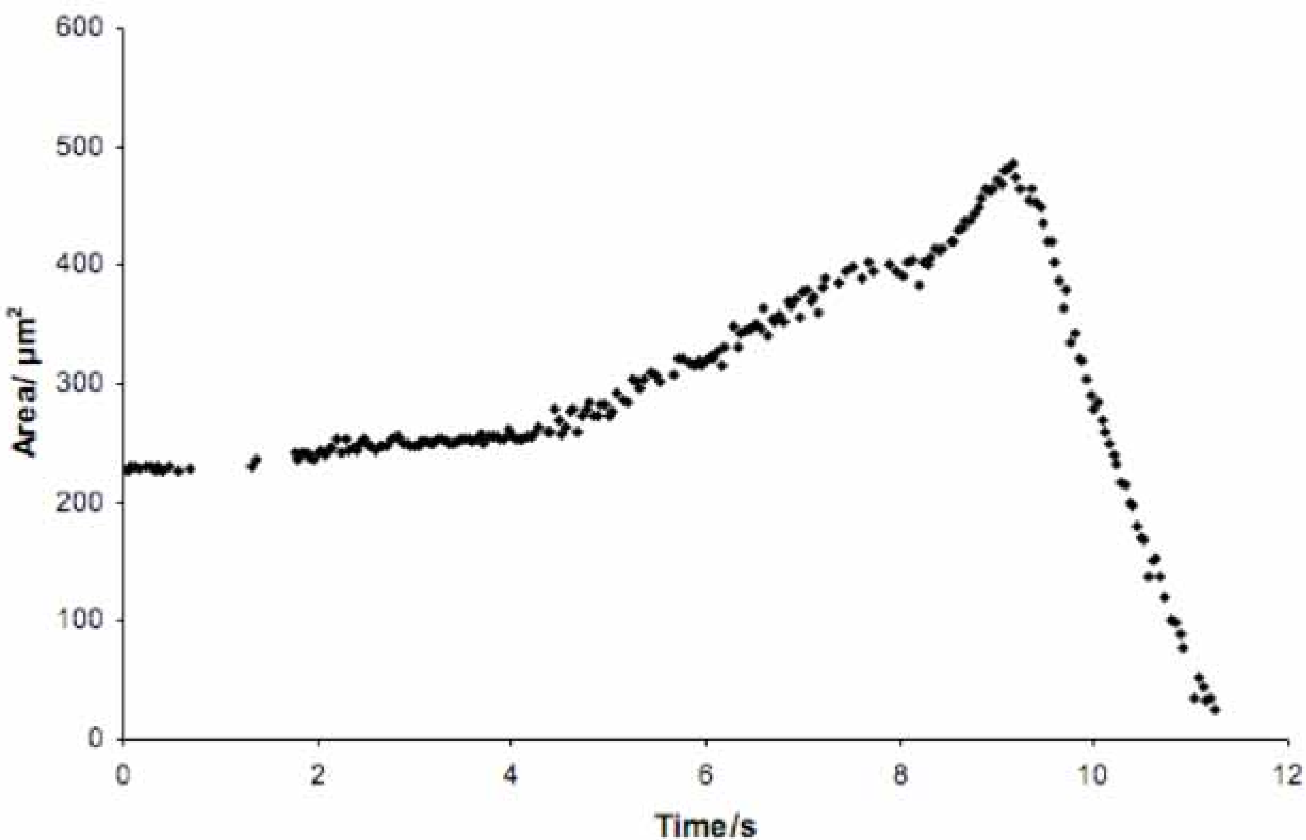


HP Martin & J Cabral et al, J Physics: Conference Series 247, (2010)

Polystyrene Sulphonate Dissolution – Direct Observations

t/s	0,04	2,36	3,2	4	4,8	5,76	6,4	8,04	8,16	8,8	9,52	10	10,8	11,24
Particle														
Processed image														





Concluding Comments

Microstructures are sensitive to local compositions and energy dissipation rates

- transient
- persistent

There are a complexity of local compositions and energy dissipation rates in Batch vessels

Short residence time mixing equipment offers precision

Still much work to do to unravel the mechanisms and kinetics

Direct observations using microfluidic techniques offer routes to valuable insights for specific systems