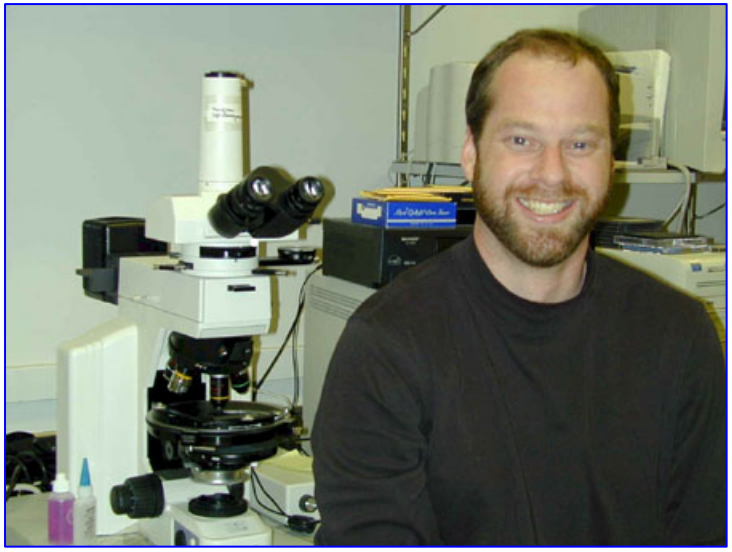
1. Effect of Colloidal Particle Polydispersity on Failure of Colloidal Gels

2. Fundamentals of Partial-Coalescence of Drops



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Executive Summary

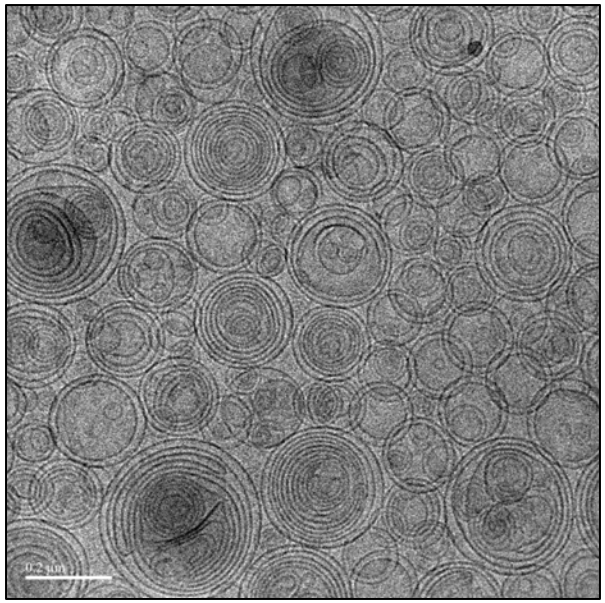
- Colloidal gels define the microstructure of materials, including consumer products
- Failure of such materials under gravitational stress can be considered a consequence of failure of all the bonds/strands along a weakest points in the gel
- In the case of homogeneous materials, we can anticipate failure through a series probabilistic expressions. In the case of heterogeneous materials, such arguments become more complicated and not well understood as event with analogues to polydispersed polymer

- Commanding/understanding control over such system requires detailed understanding the evolution (coarsening) of microstructure

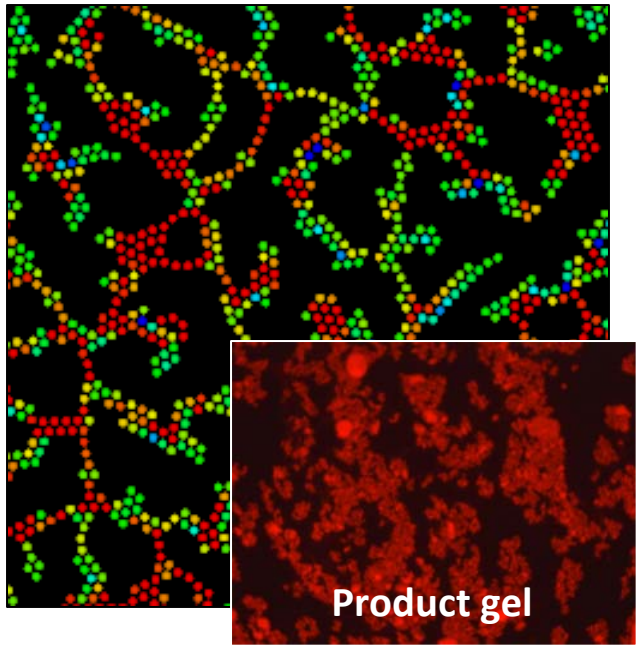
Brief Scientific Review

Product gel

vesicles gel



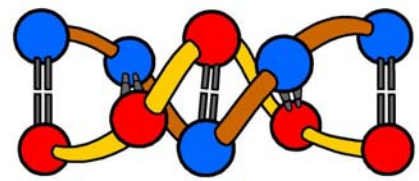
Gel cartoon



Gel structure – often dominated by fractal strands composed of many particles in a cross-section

Brief Scientific Review

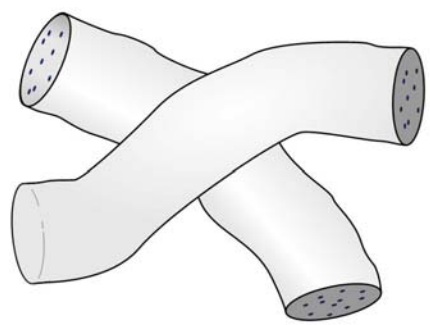
1) <u>Bond</u>- survival probability of the bond with an applied force (activated process).

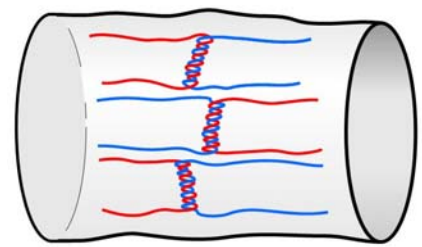


$$k_d = \omega_o \exp(-\frac{Ea}{kT})$$

$$p_1(t) = \exp(-k_d' t)$$

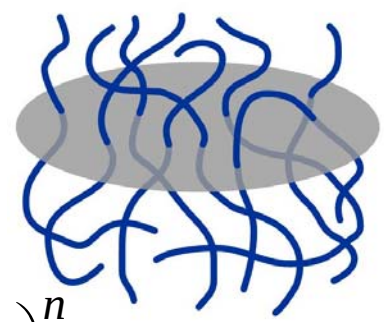
2) <u>Strand</u>- collection of bonds or particles, survival probability of these collections with applied stress





$$K_d = \frac{1}{\tau_d} = \frac{k_d}{S_n}$$

3) <u>Macroscopic Description</u>- survival probability of a collection of strands across a "failure plane"



$$\tau_d \sim \frac{1}{n^2 \sigma C k_a} \left(\frac{k_a}{k_d} \right)^n \exp(-n\sigma C)$$

Pre-print: . Sprakel et al. *Phys. Rev. Letters* **2011**

Brief Scientific Review

Creep experiments on 3 different colloidal gels (red – short ranged depletion gel, black – carbon black, green – stearylated silica). (J. Sprakel, S. Lindstroem, T. E. Kodger and D.A. Weitz, PRL 2011, accepted)

The existence of a second exponential domain at low stresses arises from the <u>reformation</u> of individual colloidal bonds within a strand, before the entire stand yield.

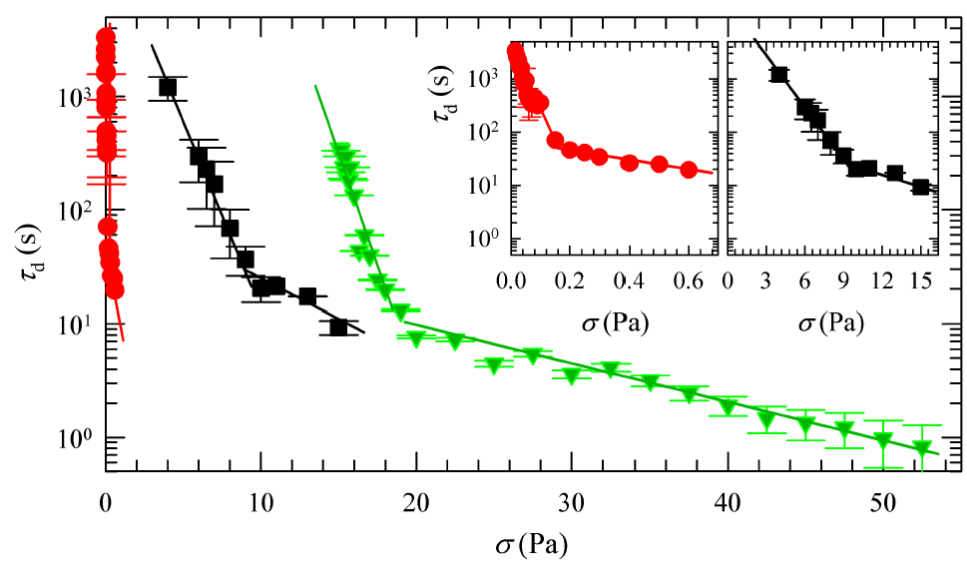
The typical yielding times range from 10^4 to 10^{10} seconds for weak to strong gel respectfully.

Low stress

$$\tau_d \sim \frac{1}{n^2 \sigma C k_a} \left(\frac{k_a}{k_d} \right)^n \exp(-n\sigma C)$$

High stress

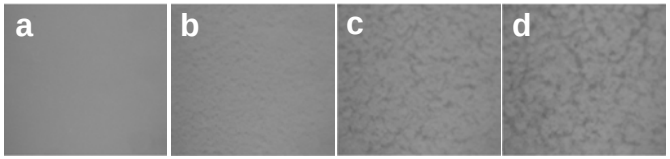
$$\tau_d \sim \frac{S_n}{\sigma C k_a} \exp(-\sigma C)$$

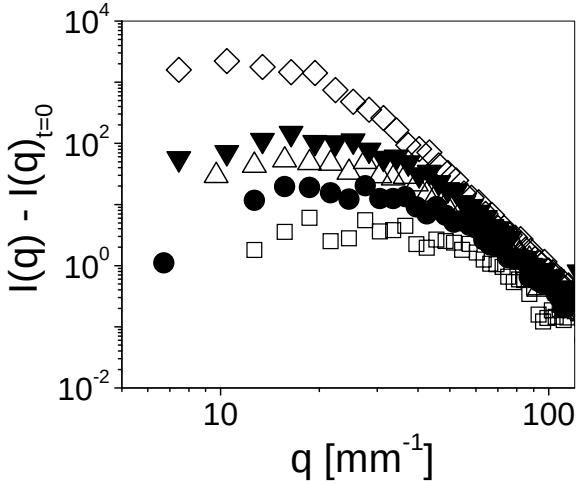


Brief Scientific Review

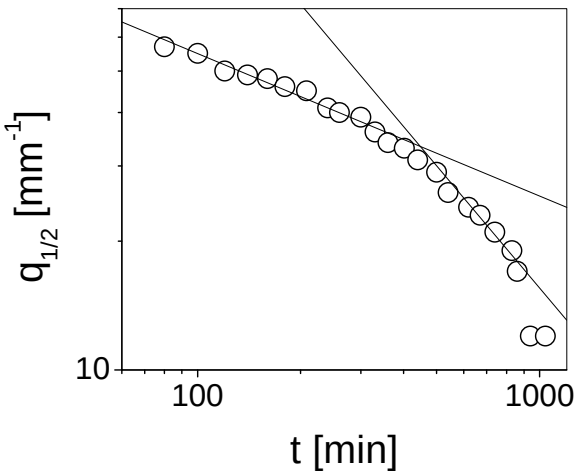
Phase separation versus gelation in colloid-polymer mixtures: The role of polymer polydispersity. J. J. Lietor-Santos et al. Langmuir, 2009

Snapshots of the coarsening process for ϕ = 0.1, c_p = 5 mg/ml,





Time dependence of q1/2



Evolution of microstructure and sedimentation behavior of gels is a function of the polydispersity of the polymer

Brief Scientific Review

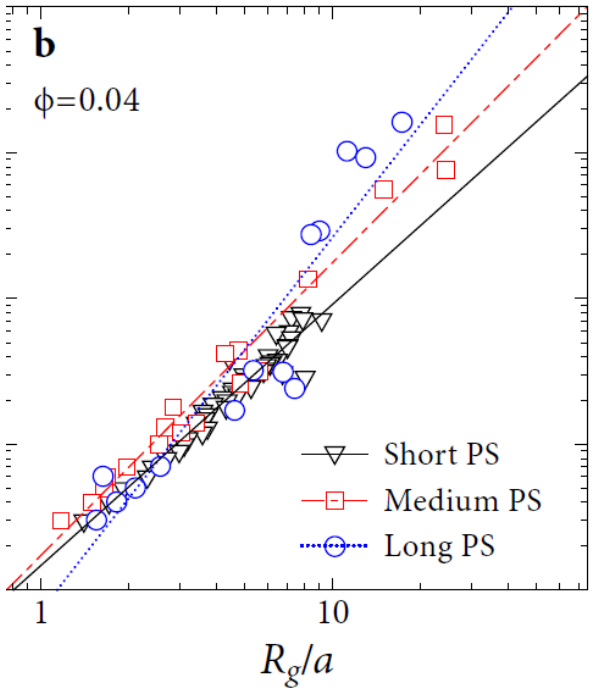
- We can also hypothesize that changing the polydispersity of the colloid affects the coarsening
- We have assumed that all bond are equal = scales with n. Stands composed of disordered bonds may couple not linearly with n, i.e.
- Polydispersity in depletant is known to affect stability (A.Fernando-Nieves, M. Lynch, et. al.)

$$\tau \neq \exp(n)$$

- More representative of real products - polydispersed
- Understanding this simple divergence from monodispersed to bidispersed, could be beneficial to increasing the shelf-life (i.e. slowing aging) of a wide variety of products simply by modifying the particle size distribution.

Relevant ground (Earth) work

- Gel structure - as a function of depletion range, the fractal dimension varies from d_f ~ 1.7 – 2.6. (P.Lu, PhD thesis)
- As a results, the average stand thickness changes, n, changes dramatically.



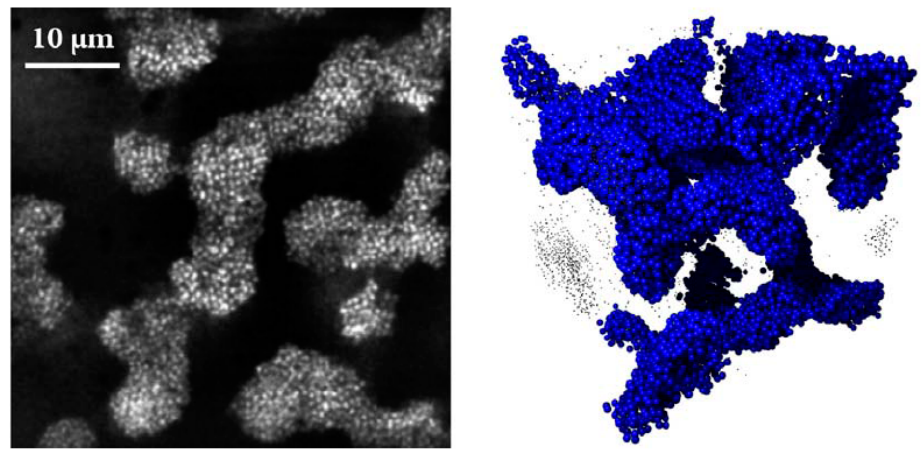


Figure 9.4: (left) 2D confocal microscope image (60 μm)^2 and (right) 3D reconstruction (60 μm)^3 of a colloid-polymer sample with $\phi = 0.15$ and long-polymer depletant, which is a spanning (percolated) gel ($c_p = 1.31$, $\xi = 0.11$, $U = 2.7$).

Justification for ISS

- The zero-stress yield time from ground based work can be many hours to days (previous slide). And many yielding events must occur for mechanical instability driven by coarsening – therefore a single experiment may take ~10-100 days.

- Colloidal gel dynamics over months are very susceptible to gravitational stress.

Proposed Experiment - Details

The rate of coarsening may be experimental observed by microscopy or scattering or both as a change in the characteristic strand length, S(q).

Depending on the technique, the molecular weight, and particle diameters can be tuned according to the relevant length scales (r~150nm for scattering, r~500nm for microscopy).

9 samples are proposed:

S1-S3: variation in the range of the potential while maintaining the reduced 2nd virial coefficient (B_2*) (see next slide for representative potentials)

S4-S7: small variations in volume fraction yield large difference in elastic moduli,

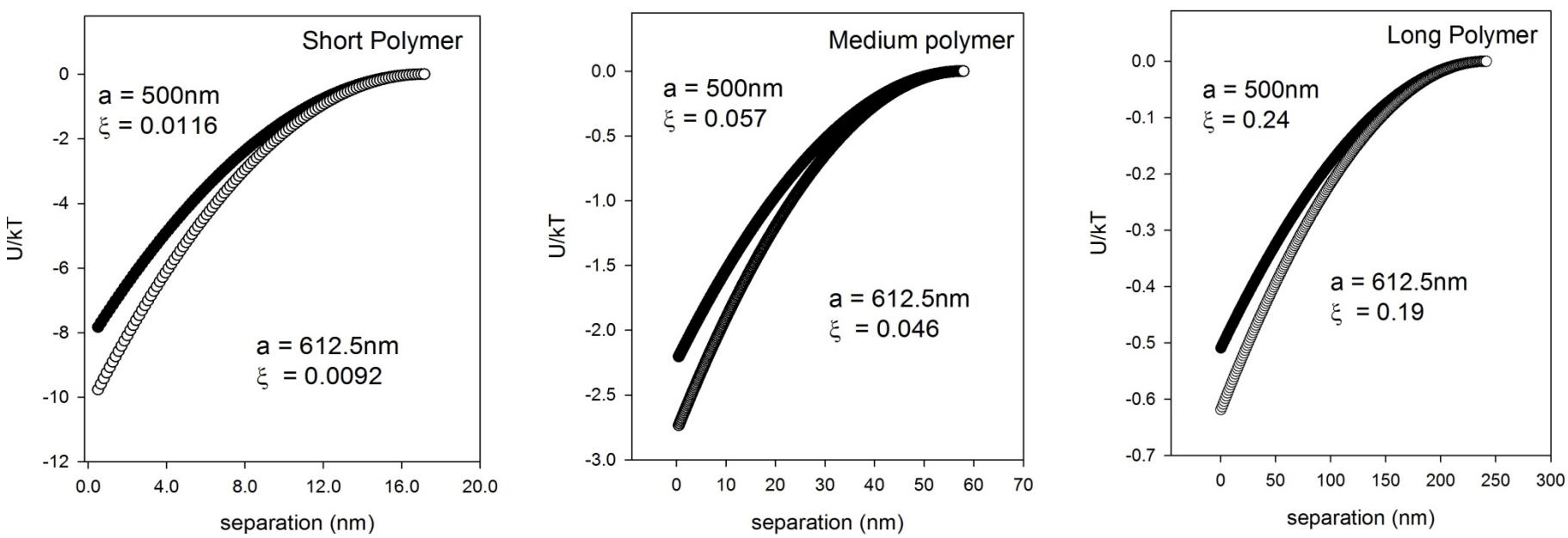
$$G'_p = G'_0 (\phi - \phi_c)^\nu$$

where ν = 2.1 for short-ranged, or ν = 3.3 for long-ranged (V. Prasad, PhD thesis). These samples would maintain the range of interaction with small variations in volume fraction (5% overall)

Proposed Experiment - Details

S8-S9: vary the colloid polydispersity. Identical to S1-S3 in range and depth of interaction, these samples would use a binary mixture of equal number with a size ratio, a1/a2 = 1.25. This particular size and number ratio has been shown to exhibit a disordered structure in binary metals (D. Miracle, Int. Mat. Rev. 2010).

Only a small bias in potential is expected toward the larger particles, due to an increase excluded volume. This small bias is not expect to affect the structure of gel only its dynamics and thus the rate of coarsening.



Success Criteria

- Direct observation of gel structure coarsening under no external stress

- Does strand thickness influence coarsening?
  (Direct implication to consumer product design)

Experiments = More realistic model of coarsening/strand dynamics

Executive Summary

Project 2 – Drop dynamics

Need to better understand the *underlying physics* that governs the stability (or coalescence) of emulsion and/or squishy drops- partial coalescence.

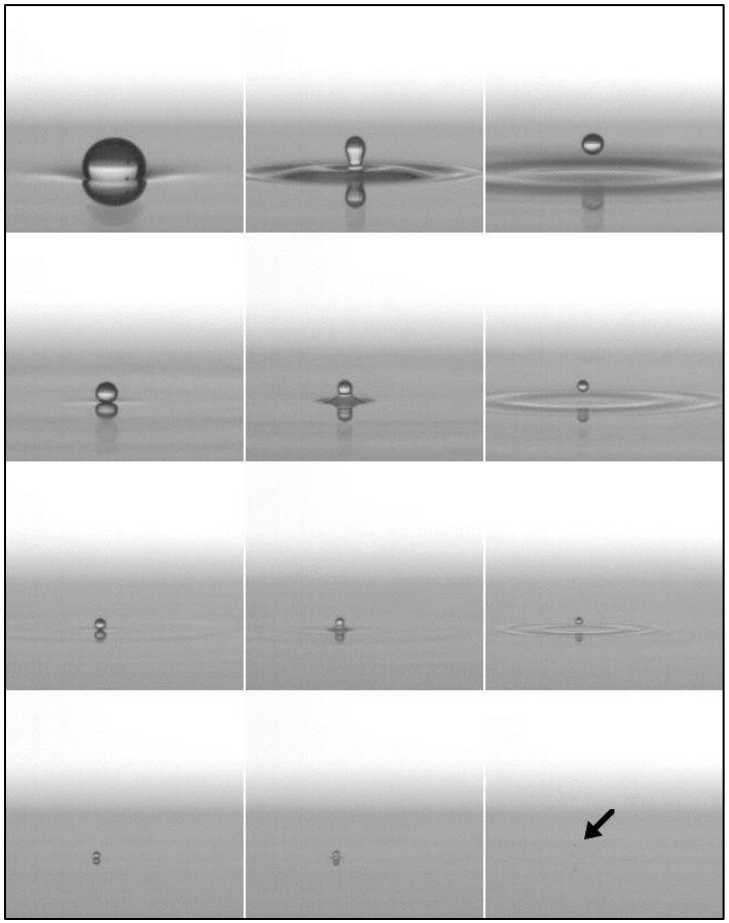
Fundamental to:

- Production and stability of consumer products
- Particle manufacturing, medicinal chemistry, physiology, oil recovery and natural processes such as rain and ocean spray.

Technical Goal: better understand the factors that govern drop coalescence/partial coalescence

Reaching Goal: path forward for explore soft drops in future experiments- proof-of-concepts

Droplet Cascade



Scientific Overview

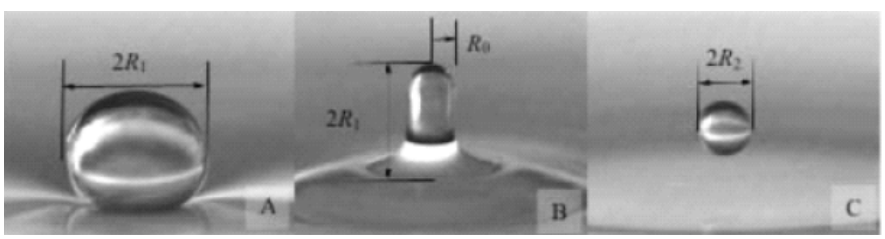
Generally accepted physics

Lubrication Forces for approaching drops; restitution

Disjoining Pressures at very small distances, where molecular force matter

Spontaneous formation of a 'neck'… The race begins

Necking of the drop*



Debate/Discussion

- Rayleigh instabilities
- Capillary waves
- Rockets- mass transfer!

Current best thought

Partial coalescence is primarily driven by mass transfer, although more complex

Dynamics

Drainage versus pinch off rates

*Honey et al. Phys. Rev. E 73, 027301 (2006)

Relevant ground (Earth) work

Experimental

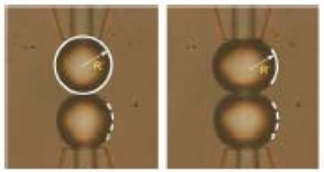
- Drops on to interfaces
- Drops-to-drop measurements
- Different fluids
- Vertices

Modeling

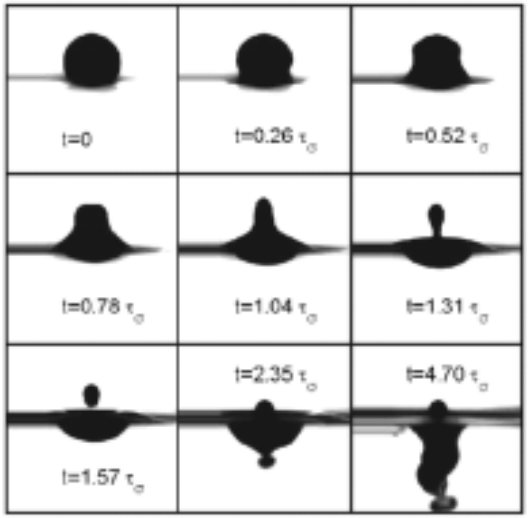
- Deformation of drops on approach
- Hydrodynamic approaches to neck closure
- Modeling vortices

Good basis to understand the problems, but should be able to remove many challenges in the analysis of the experiments

Dueling Drops

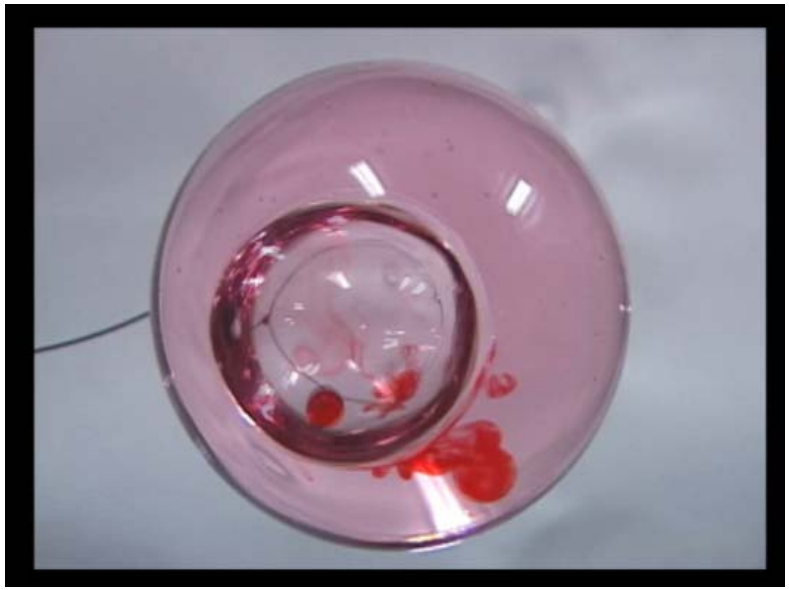


Drops in two different fluids

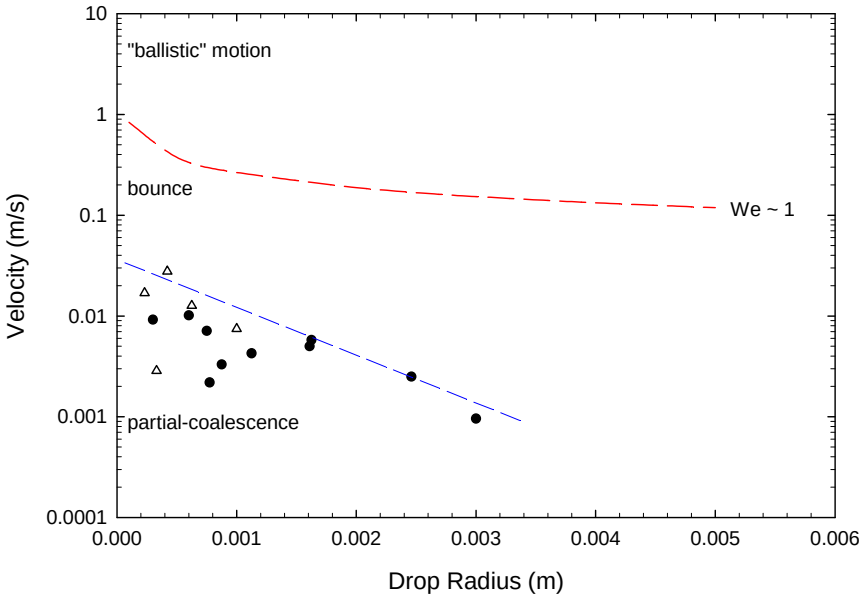


Relevant ground (microgravity) work*

Partial coalescence of the drops in microgravity



Regimes of drop behavior



* Donald Pettit- NASA

Justification of ISS

- Clarity in data, allowing exceptional ability to analyze movements

- Liquid-liquid systems will take a long time to equilibrate and need to remove sedimentation

Experiment (perspective)

Fundamental challenge for experiment with soft colloids

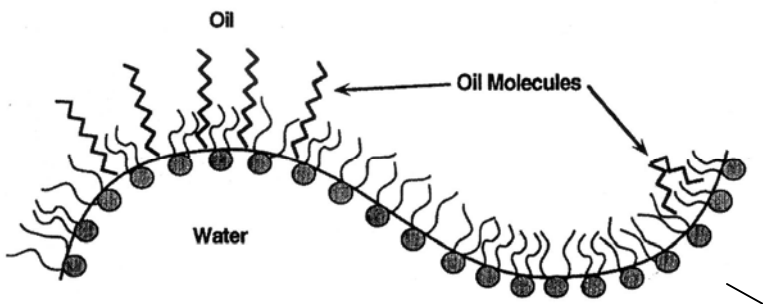
• *Preparation:* how can drops be created, as it is hard to believe the drops will survive storage, launch and long-term storage

• *Stability*: time (change) << time (storage)

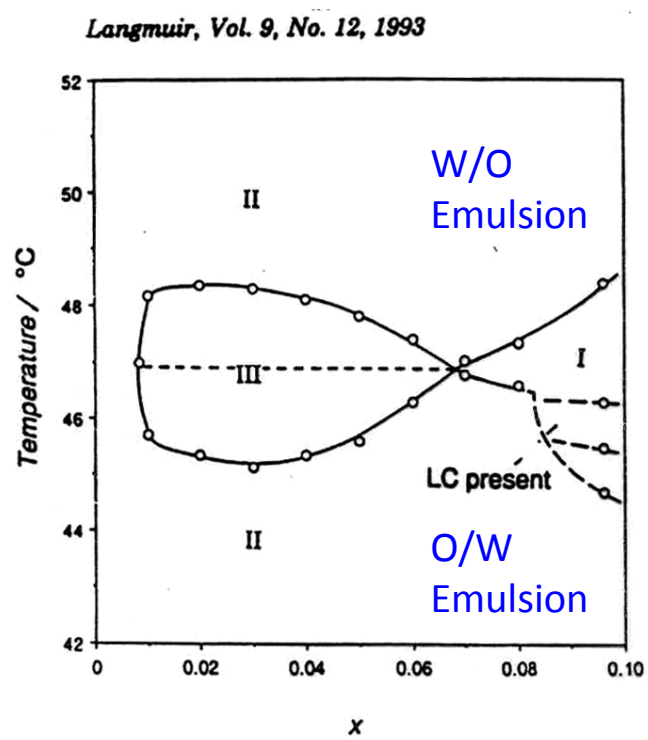
• *Experiments*: small number of samples but a large number of experiments.

Experiment

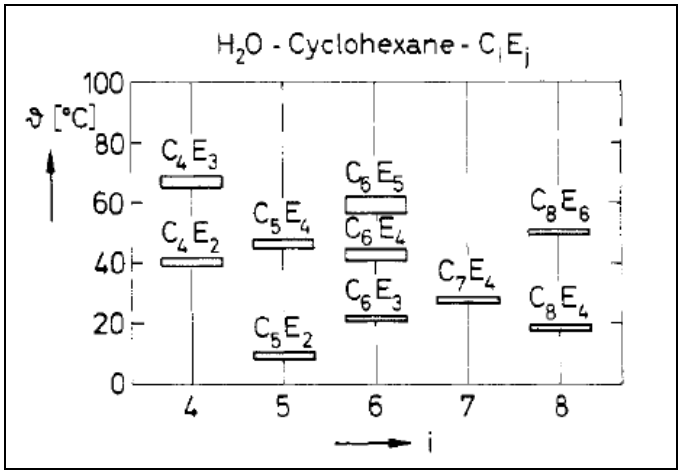
Oil-water interface



Phase behavior

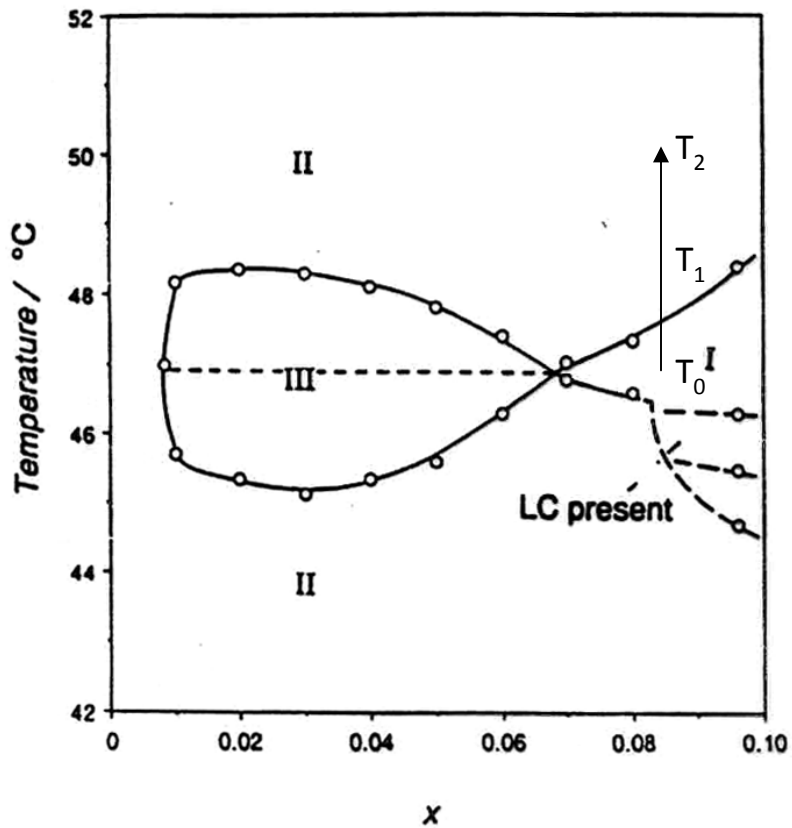


Water/ Heptane/ $C_{12}E_6$



Kahlwiet et al J. Phys. Chem. 1983, 87, 5032-5040

Experiment



Proposal

1. Start experiment in 1-phase microemulsion region (T_0)
2. Adjust temperature (T_1) to create emulsion drops with γ_1
3. Measure coalescence and partial-coalescence events with microscopy (traditional/fast camera)
4. Re-set Experiment (T_0)
5. Adjust temperature (T_2) to create new drops with γ_2

S10- water-cyclohexane-C4E2? Where the temperature range of the transitions fall within the acceptable range of the system

Success Criteria

- Initial ‘proof-of-concept’ experiments, to determine whether this is a viable approach to producing and studying drops in microgravity

- Sort through the data to determine whether it is possible to quantify the parameters to understand partial-coalescence.

↓

- Rayleigh instabilities
- Capillary waves
- Rockets- mass transfer