

Delayed sedimentation: From formulation to physics and back again

Alan Parker
Corporate Research Division,
Firmenich SA
Geneva
Switzerland

Define a fast, scientifically based test to predict when the effects of gravity will make a sample unacceptable



Overview

- Preliminaries
- Phenomenology
- Towards a theory
- A rheological correlate?



A little history

1. Alex Lips (Unilever, 1995): “No polymeric stabilizer that works for 10% emulsions”
2. Folk lore: “Xanthan is a good emulsion stabilizer because it has a yield stress. Add it and emulsions acquire the yield stress”
But it doesn't have a yield stress at practical concentrations ☹️
3. Project with IFR Norwich ⇒ “How does xanthan stabilise salad dressing?” (1997)

Defining the playing field

- Only concerned with colloidally stable dispersions:
Particle size distribution is constant
- Only concerned with weakly (depletion) flocculated dispersions
- Only interested in samples without visible creaming or sedimentation:
Once it has destabilized – throw it out



Defining the playing field

- Use practical systems:
 - 1) Polydisperse: solution must be robust and broadly applicable
 - 2) Particles are large enough to cause problems – large Peclet number



$$Pe = \frac{vl}{D}$$

Stokes' velocity v Sample height l

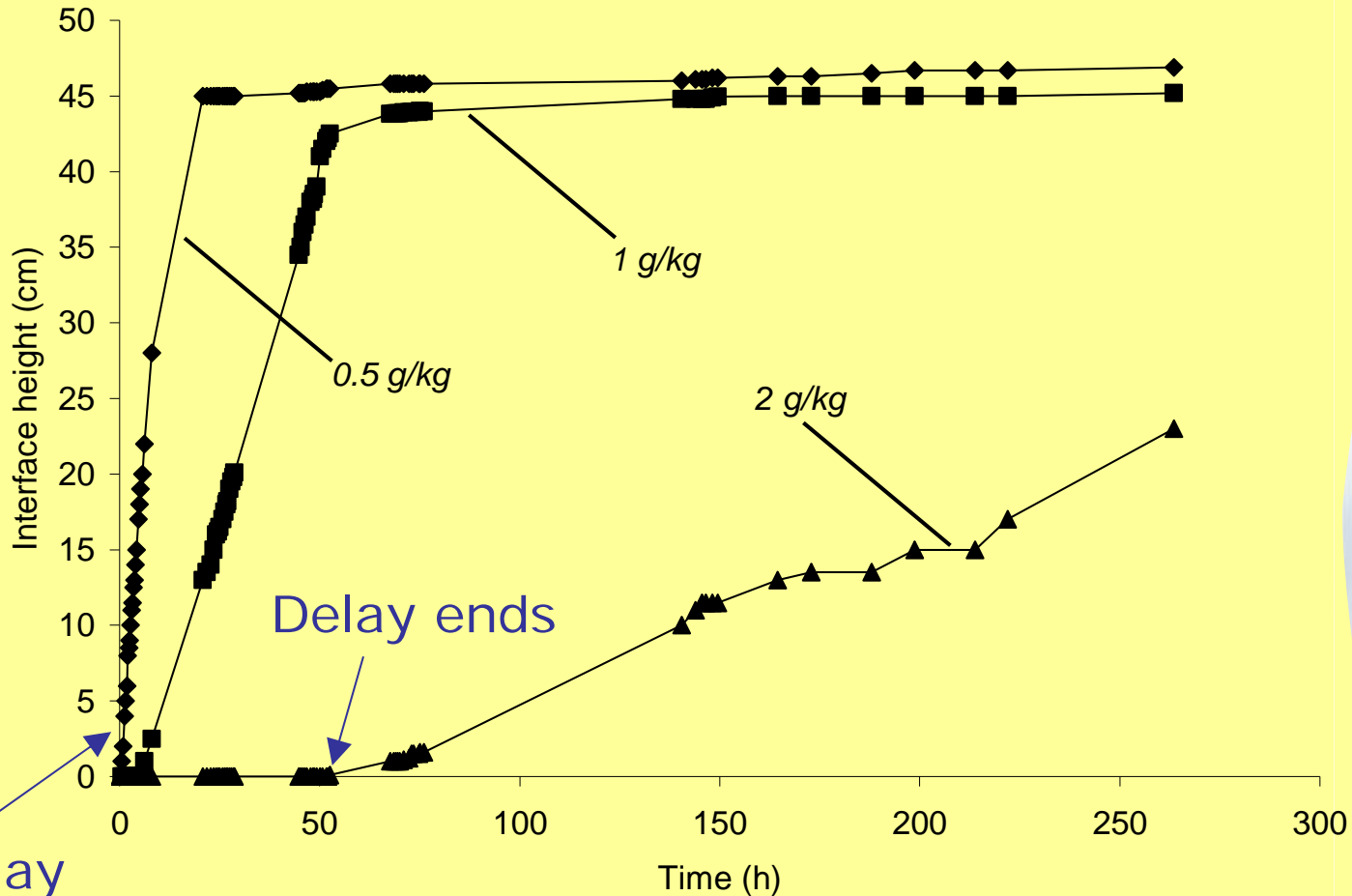
Diffusion coefficient D

What *is* the effect of adding xanthan to an emulsion?

- Mix stable emulsion with xanthan solution
- Emulsion – alkane+2% Tween 60.
Diameter = polydisperse: 0.1-10 μm
- Vary emulsion fraction & xanthan concentration
- Track the interface height as a function of time



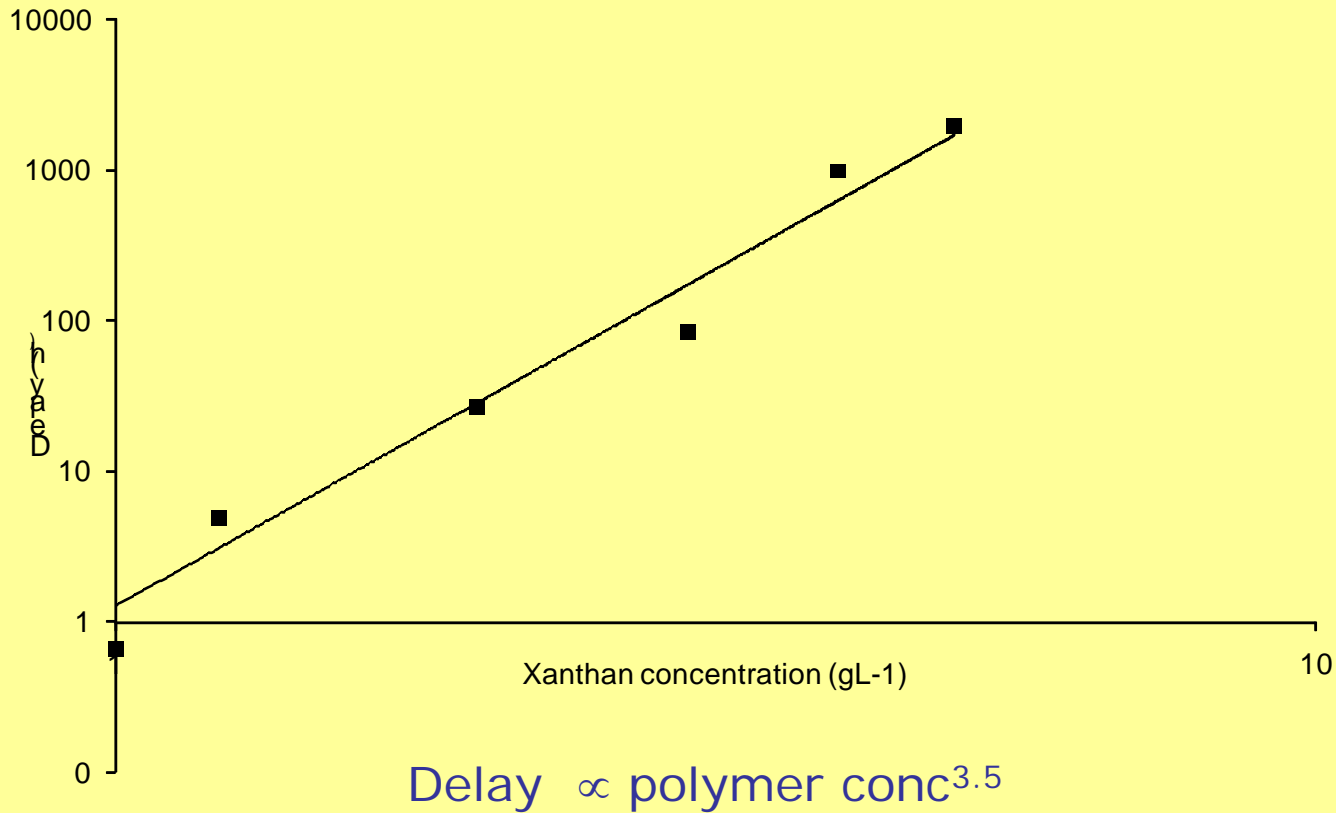
Creaming can be *delayed*
Neither *immediate* nor *absent*



No delay

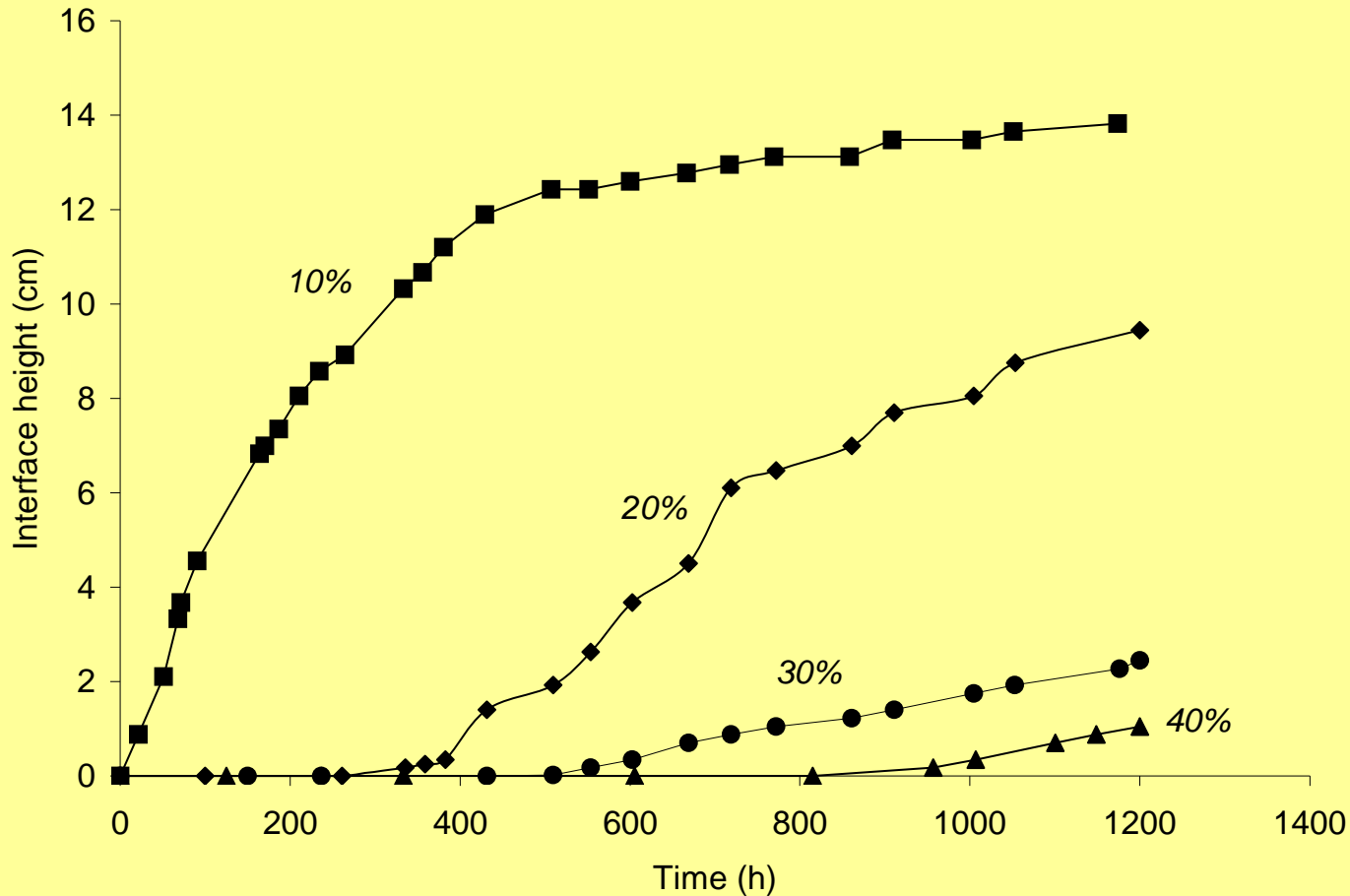
Delayed creaming essentials

More polymer = Longer delay



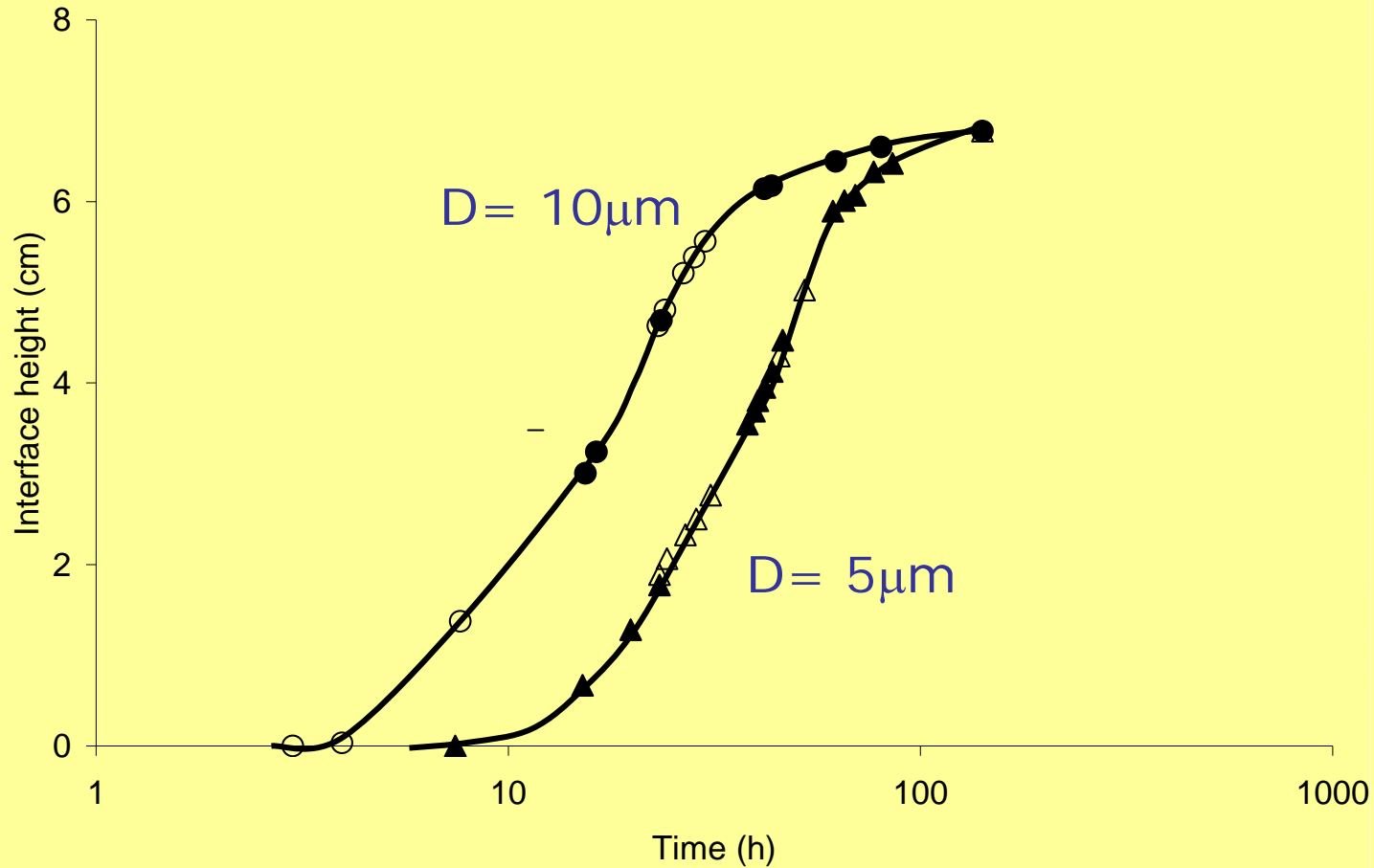
Delayed creaming essentials

Higher volume fraction = Longer delay

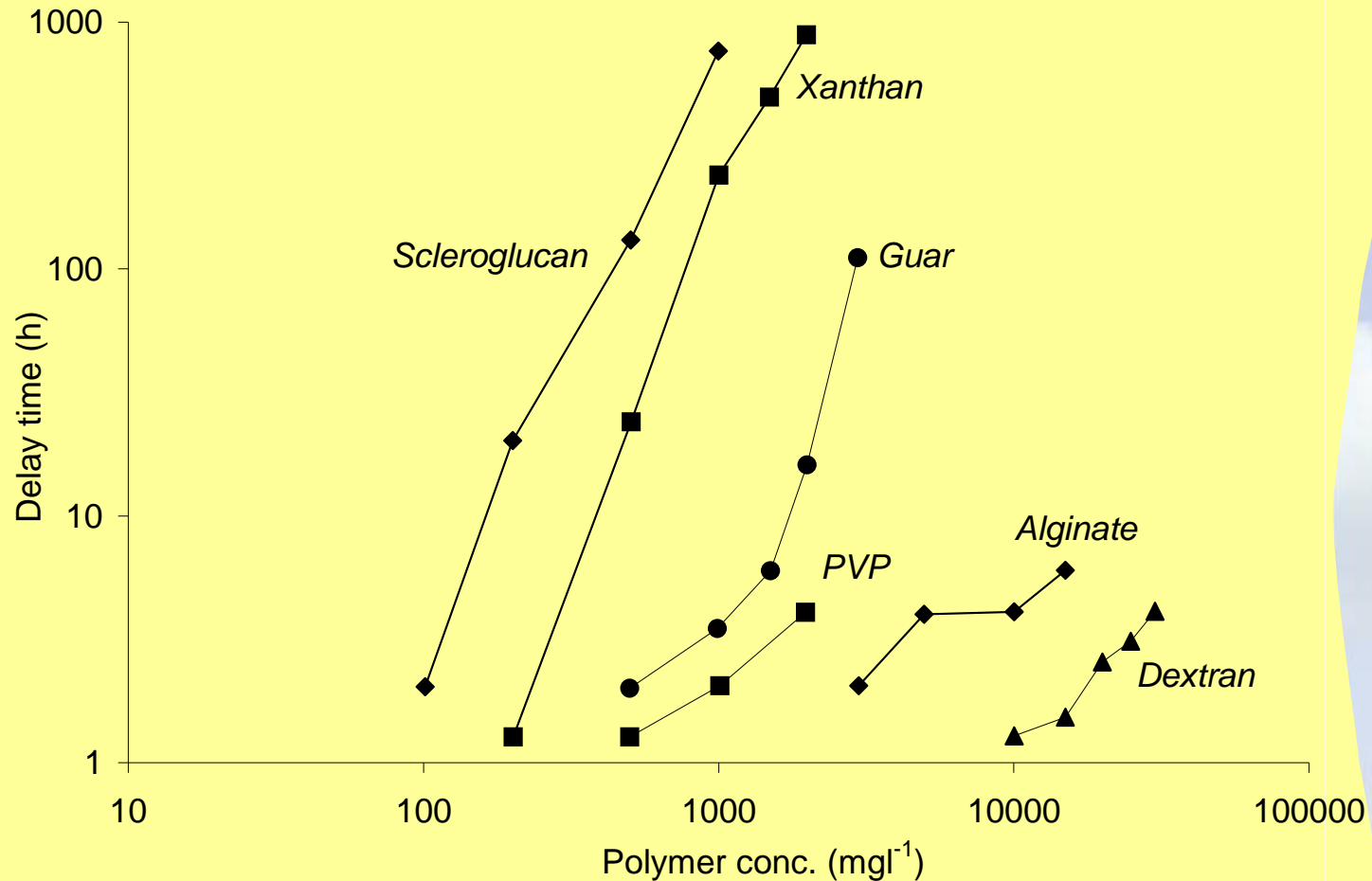


Delayed creaming essentials

Smaller droplets = Longer delay

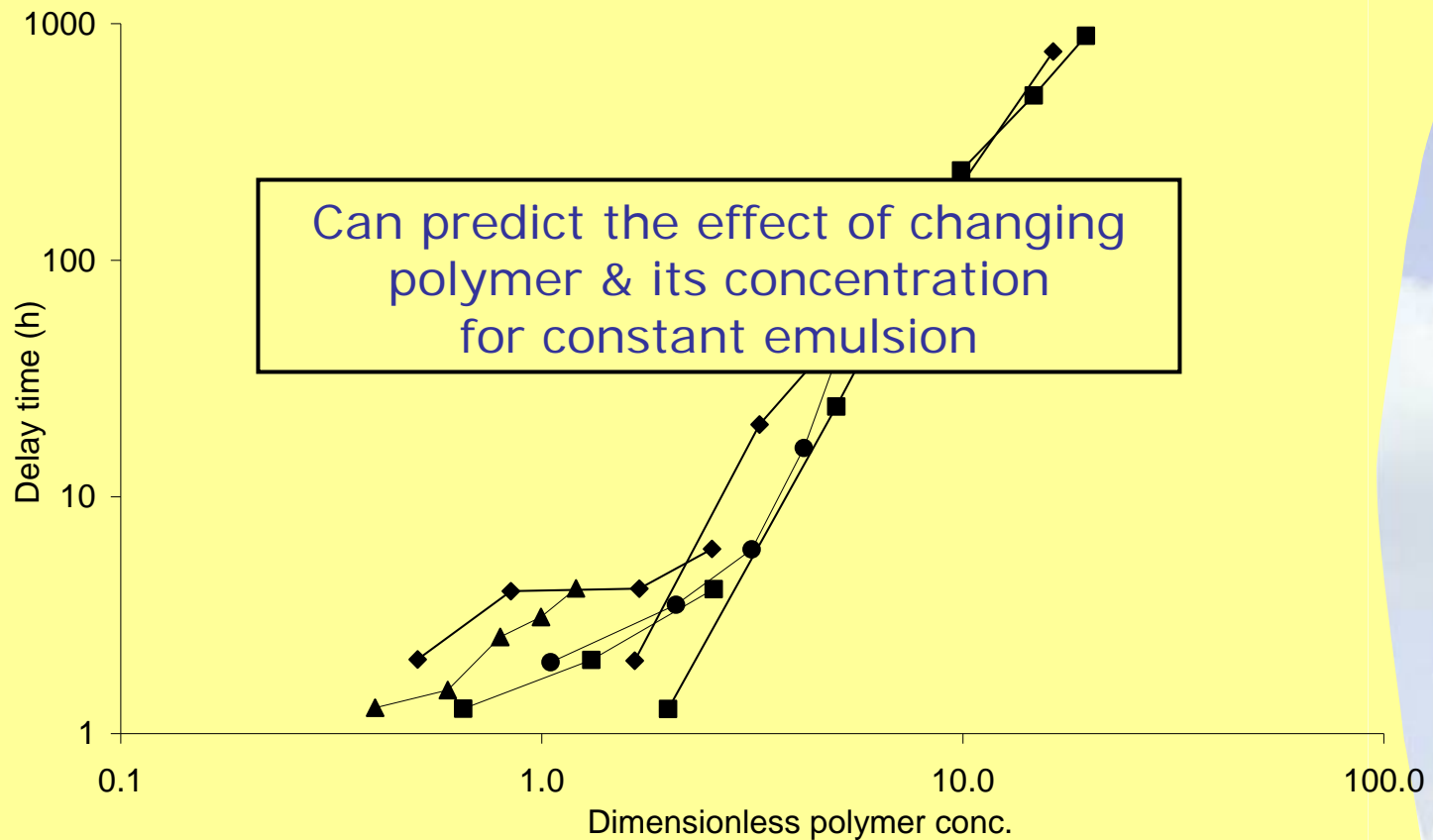


Make the polymer concentration dimensionless:
Multiply by the intrinsic viscosity
= hydrodynamic volume/unit mass



Delayed creaming – change the polymer

Polymer volume fraction \Rightarrow master curve



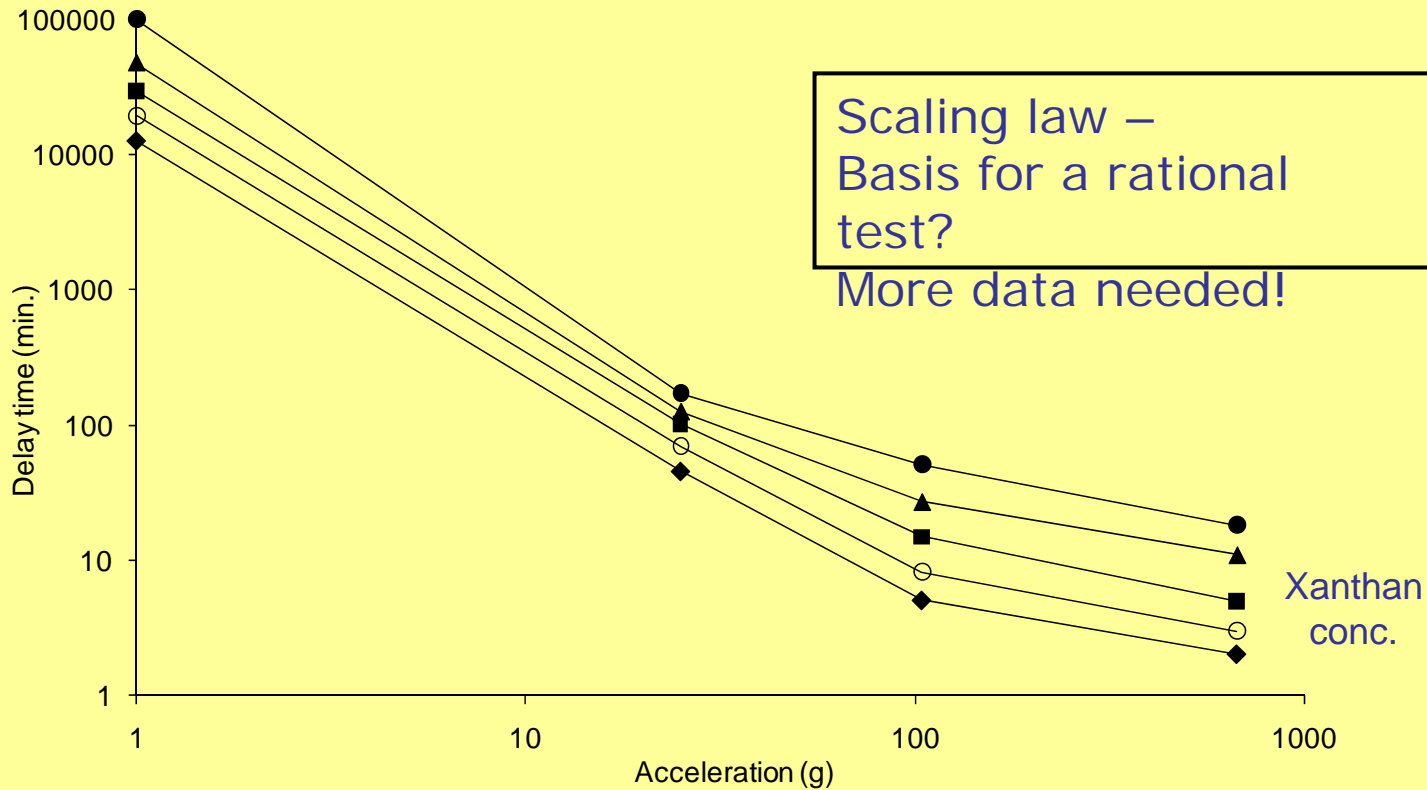
Can we see delayed creaming in a centrifuge test?

- Use a normal centrifuge
- Swing-out rotor \Rightarrow gravitation is axial
- Procedure:
 - 1) Centrifuge
 - 2) Check: Has creaming started?
 - 3) If No: Centrifuge again
 - 4) If Yes: Goto next sample
- Plot delay time in the centrifuge against delay time on the shelf



Delayed creaming essentials

Increased gravity = Shorter delay



Delayed creaming essentials

Effect of sample dimensions

1. Sample height gives the maximum gravitational stress:

$$\tau_g(\text{max}) = \Delta\rho \cdot \phi \cdot g \cdot h$$

2. Sample width can reduce the effect of gravity, if wall friction is high:

$$\tau_g(\text{max}) = \Delta\rho \cdot \phi \cdot g \cdot h - \text{wall stress}$$



Towards a theory

“Jammed” systems are trapped far from equilibrium

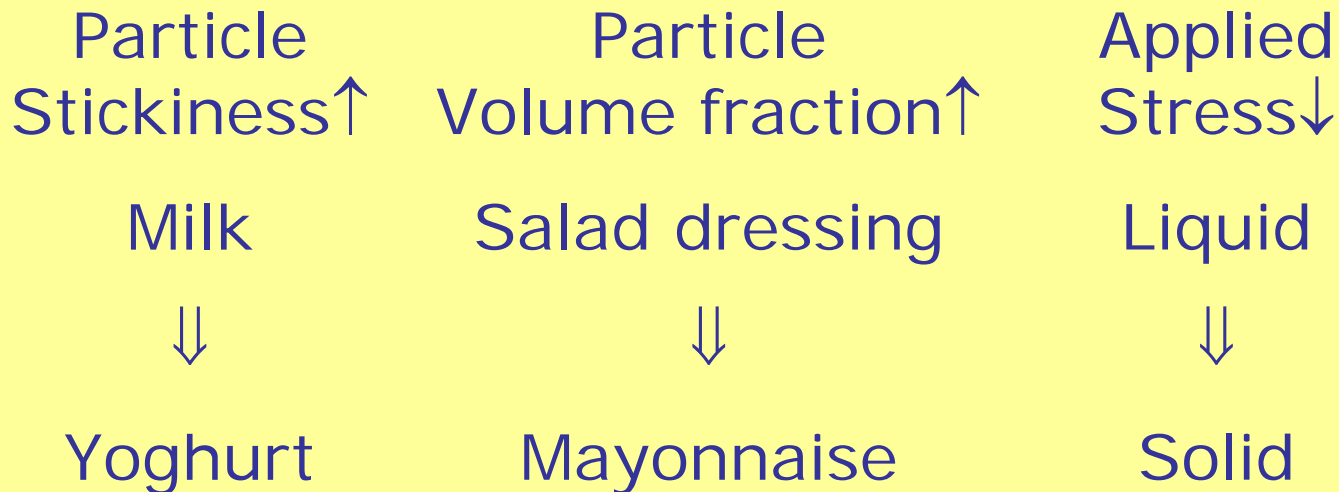
- Window glass
- Physical gels – fruit jam
- Colloidal gels - yoghurt
- Powder blocking a pipe
- Traffic jam

“These systems share key properties & can be understood within a shared theoretical framework”



The jamming paradigm for colloidal gels

Equivalent jamming effects caused by:



Same trends in delayed sedimentation
Except that, in this case, time matters
In "classic" jamming, time is absent

Towards a theory

Understanding the delay phase

During the delay phase,
vertical cracks or channels grow slowly.

The end of the delay occurs when
flow can occur from top to bottom
through the crack or channel

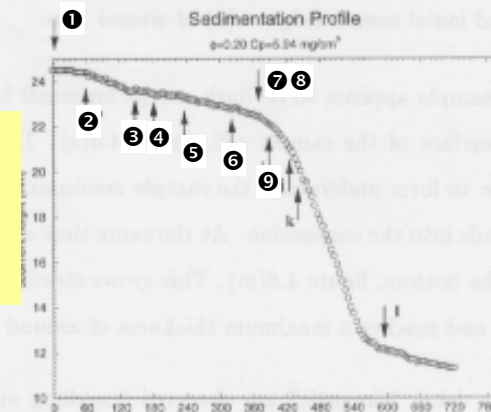
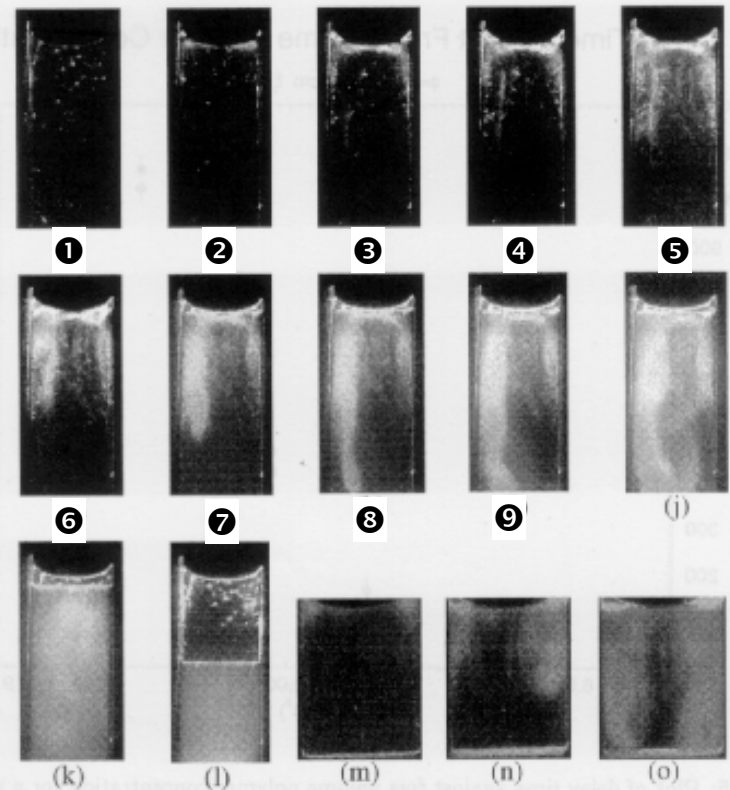


Slow channel formation

from Laura Starrs' thesis, 2001
(Physics, Edinburgh)

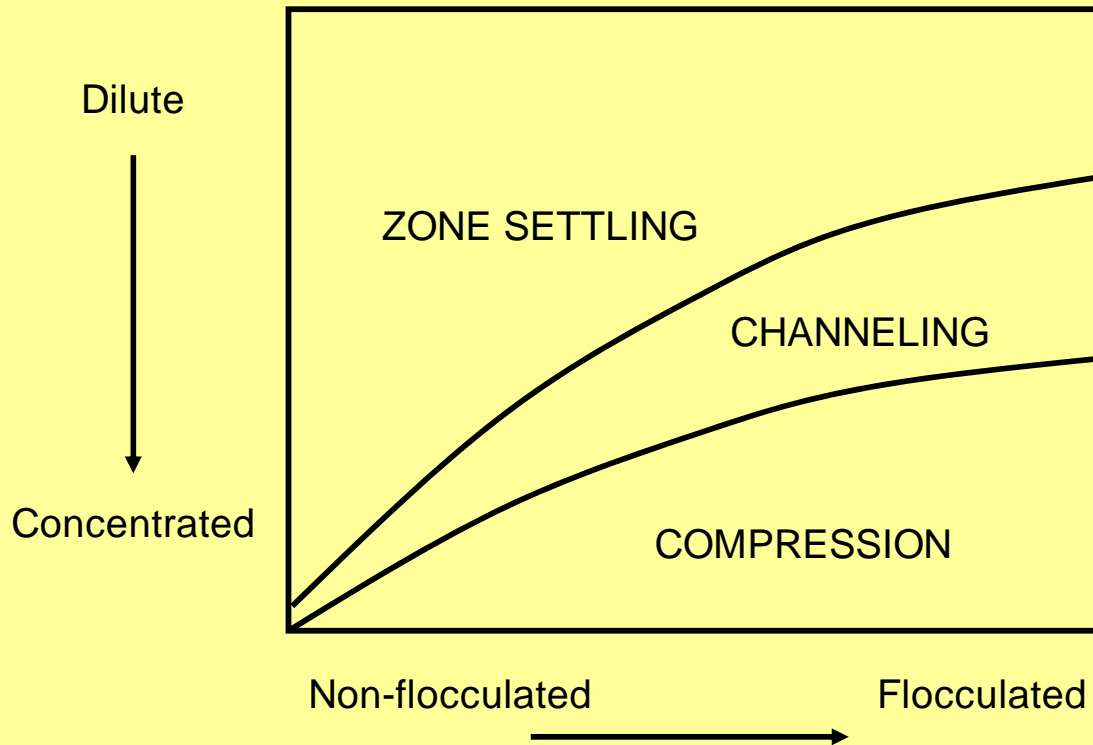
- Richard Buscall assumes:
- 1) Structure is weakening due to thermally driven particle hopping
 - 2) Channel forms when structure is weak enough

↑
Sediment height



Time→

Chemical engineers have seen channel formation during sedimentation too



Adapted from Fitch (1962)

A rheological correlate with delayed sedimentation?

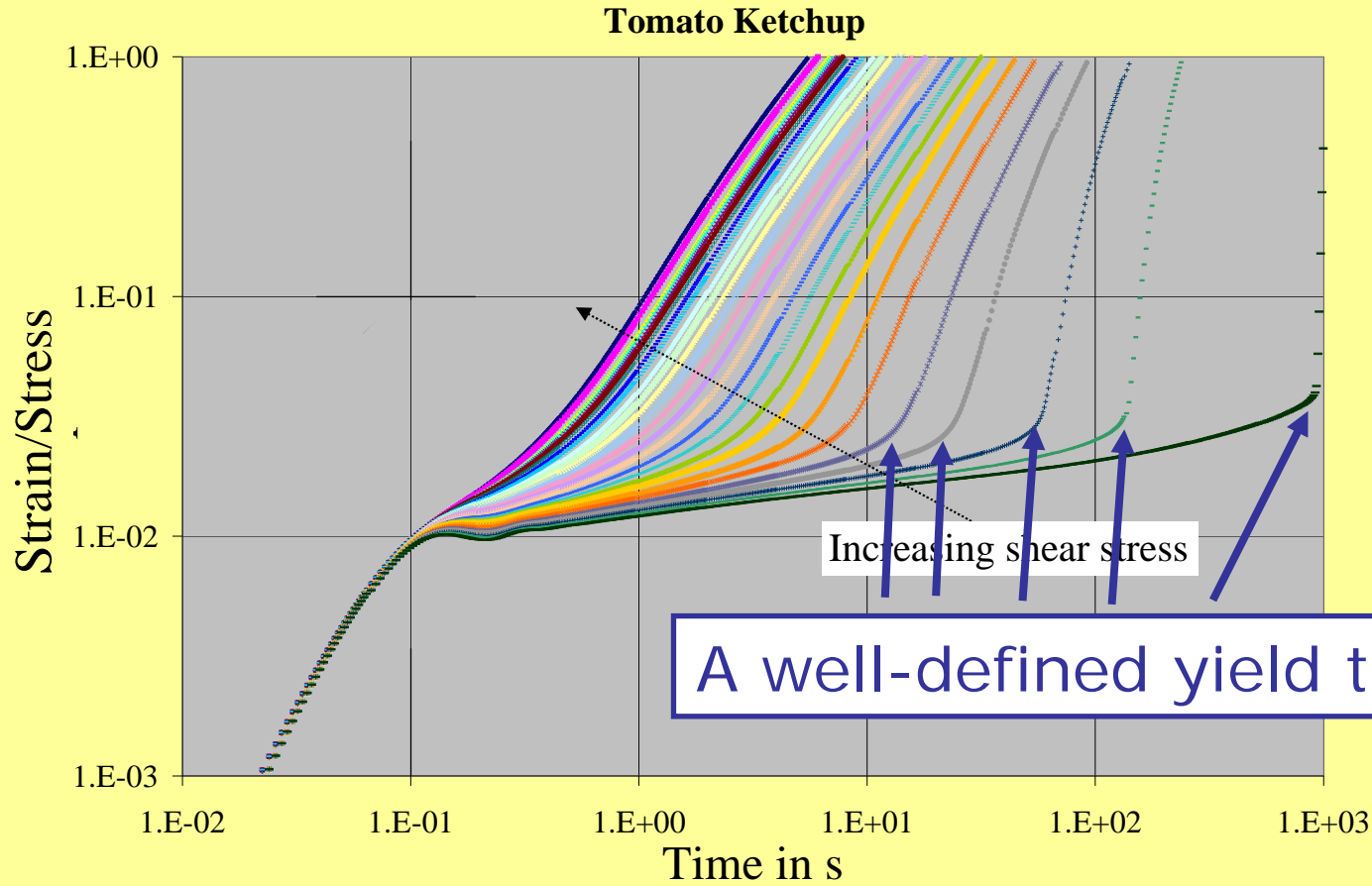
How do samples yield close to the “yield stress”?

Yield cannot be *zero* for stress < “yield stress”

Yield cannot be *instantaneous*
for stress > “yield stress”

Look more closely at the solid/liquid transition:
Measure creep curves for a series of samples of
familiar yield stress fluids...

Creep curves for increasing applied stress



From Caton & Baravian, 2006

A rheological correlate with delayed sedimentation?

Similar results for: Mayonnaise, yoghurt,
mustard, hair gel, Carbopol solution

Others find yield time scaling for model
silica+polymer & concentrated surfactant

It is tempting to make an analogy
between yield time and delay time

Need to measure both on the same
system...



Summary: Time dependence of sedimentation and creaming

Immediate – use modified Stokes' law

Delayed - Temporary Jamming

← You are here?

"Permanent" - Jamming

Our formulations are doubly constrained:

Too liquid: Not gravitationally stable

Too solid: Cannot pour / pump / print ...

Thank you for your attention

Any questions?

