The colloid crunch: fighting gravity

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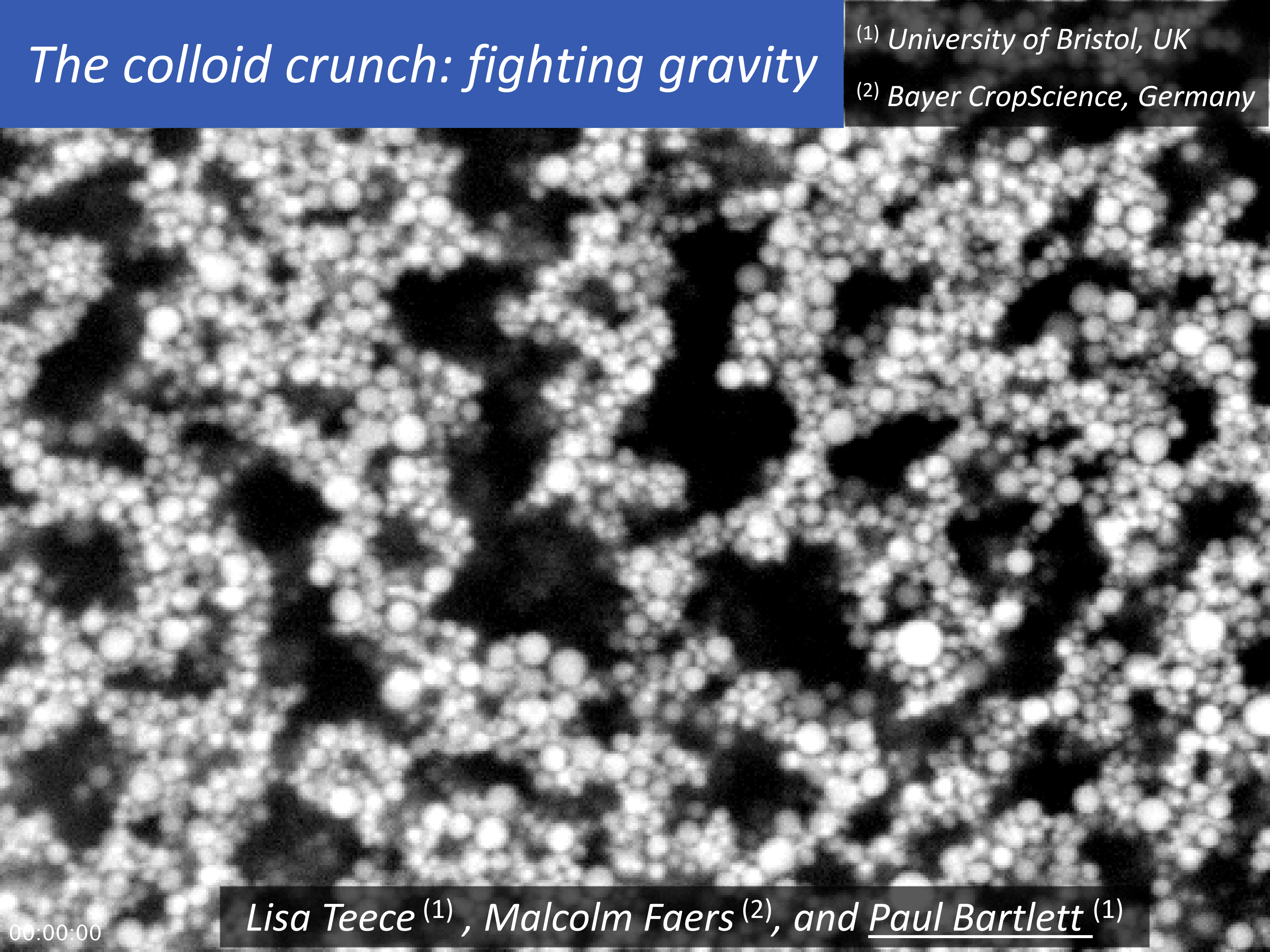
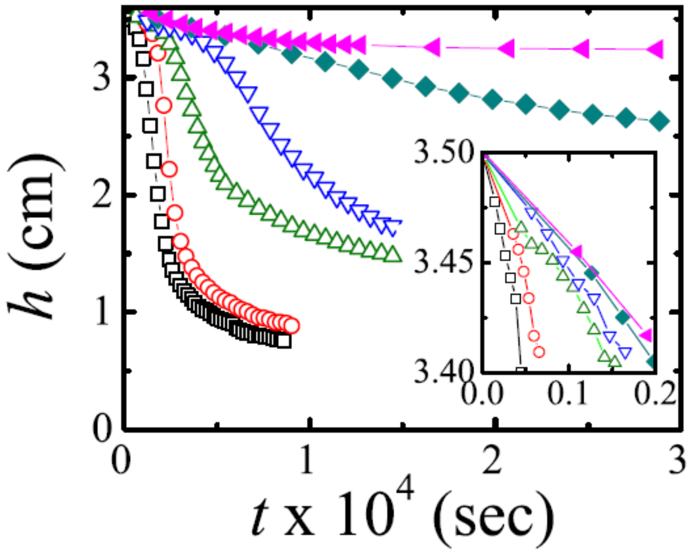


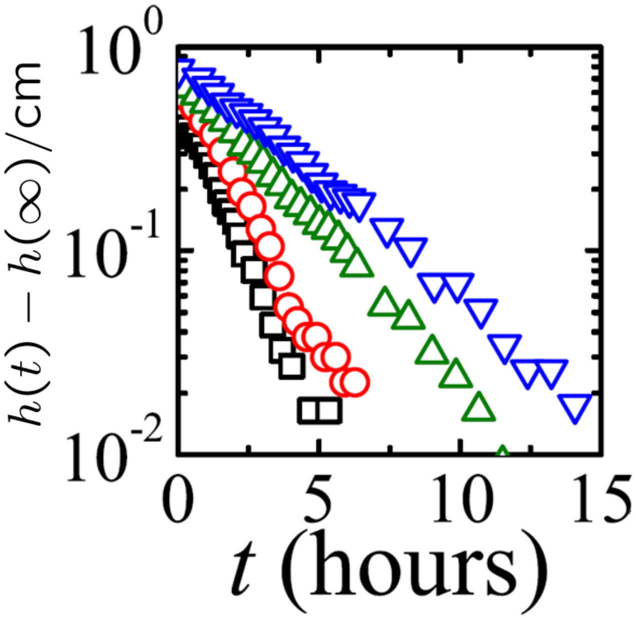
Outline of talk

- **Collapse of weak gels**
  - *A novel mechanism of collapse*
  - Switch to conventional (linear) collapse at small initial heights
- **Why?**

Collapse of strong gels

$$-U_0/k_BT \gg 10$$





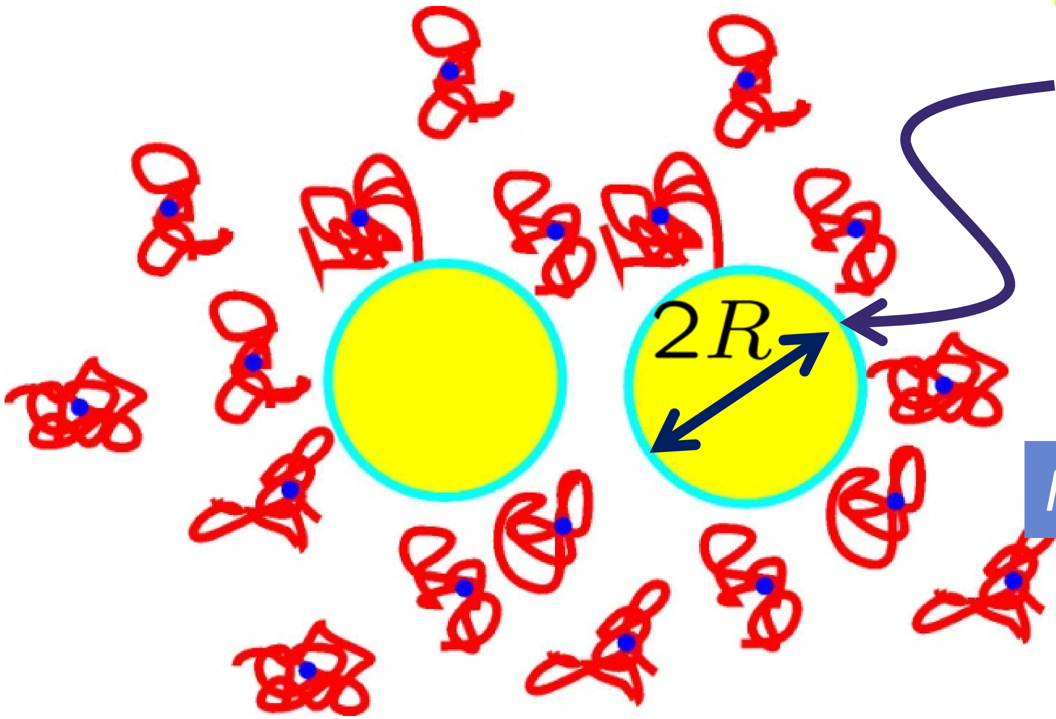
Manley et al. Phys. Rev. Lett. 94, 218302, (2005)

Buscall , Colloids Surf. 5, 269, (1982)

- Settling starts immediately.
- *Linear collapse*

$$\Delta h(t \to 0) \sim t$$

Depletion-based emulsion gel



PDMS emulsion

stabilised by mixture of nonionic and anionic surfactants

$$R = 270 \pm 25\text{nm}$$

Index-matched solvent mixture

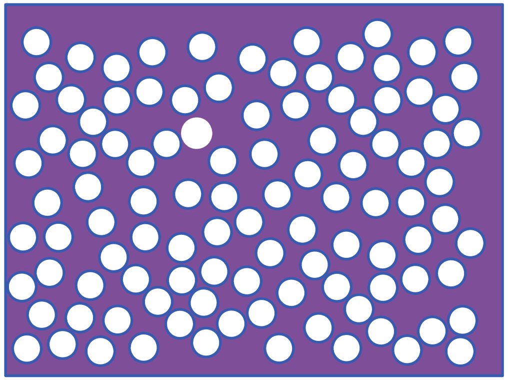
Ethylene glycol and water

$$\phi_{EG} \sim 0.56$$

Non-adsorbing polymer

Semi-dilute solution of xanthan – high molecular wt. polysaccharide

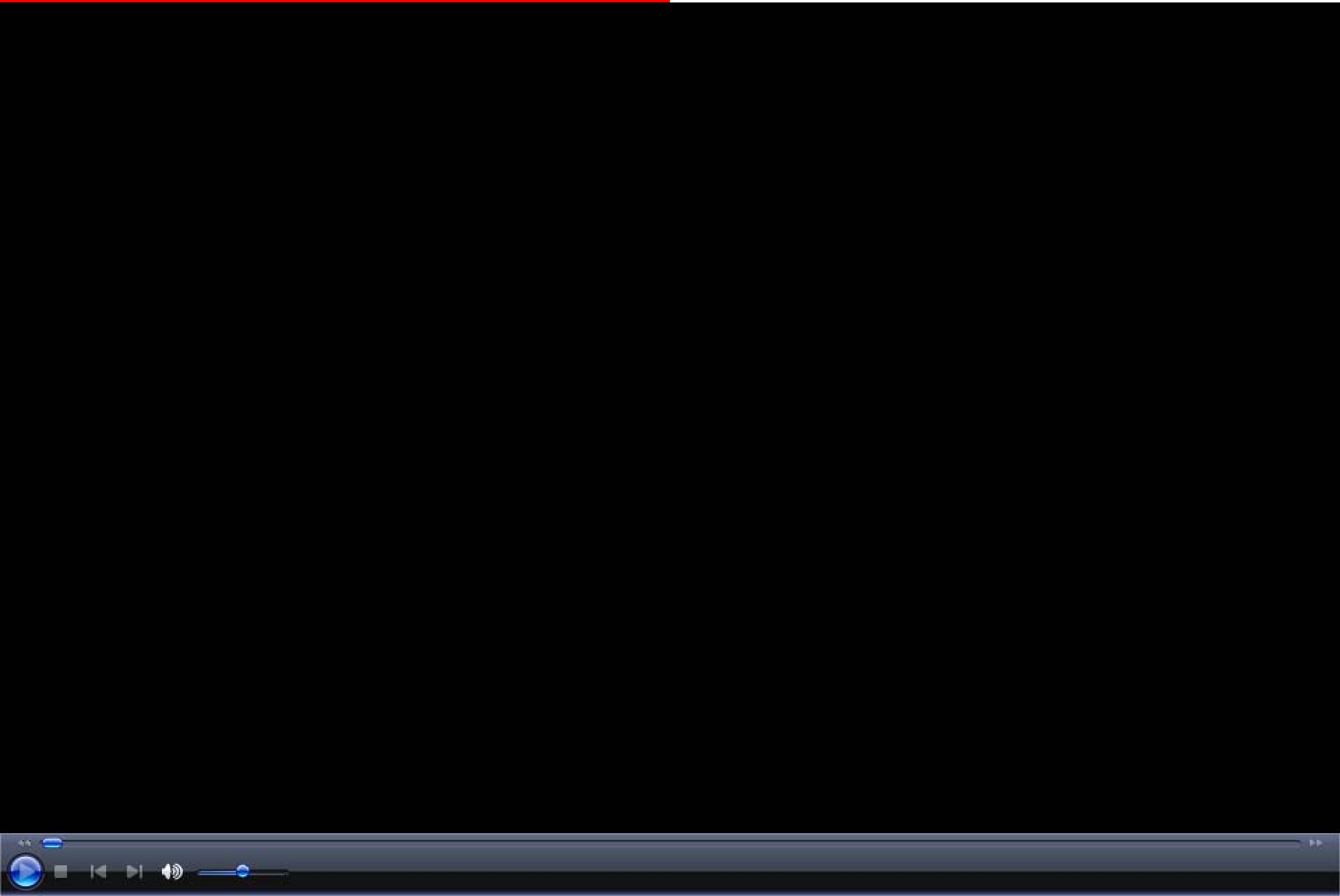
$$R_g = 264\text{nm}$$



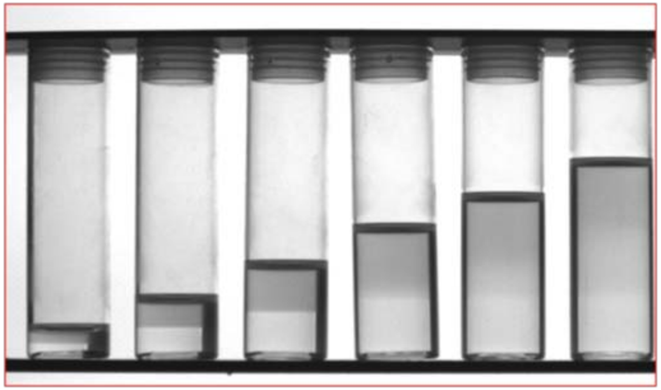
Solvent fluorescently labelled

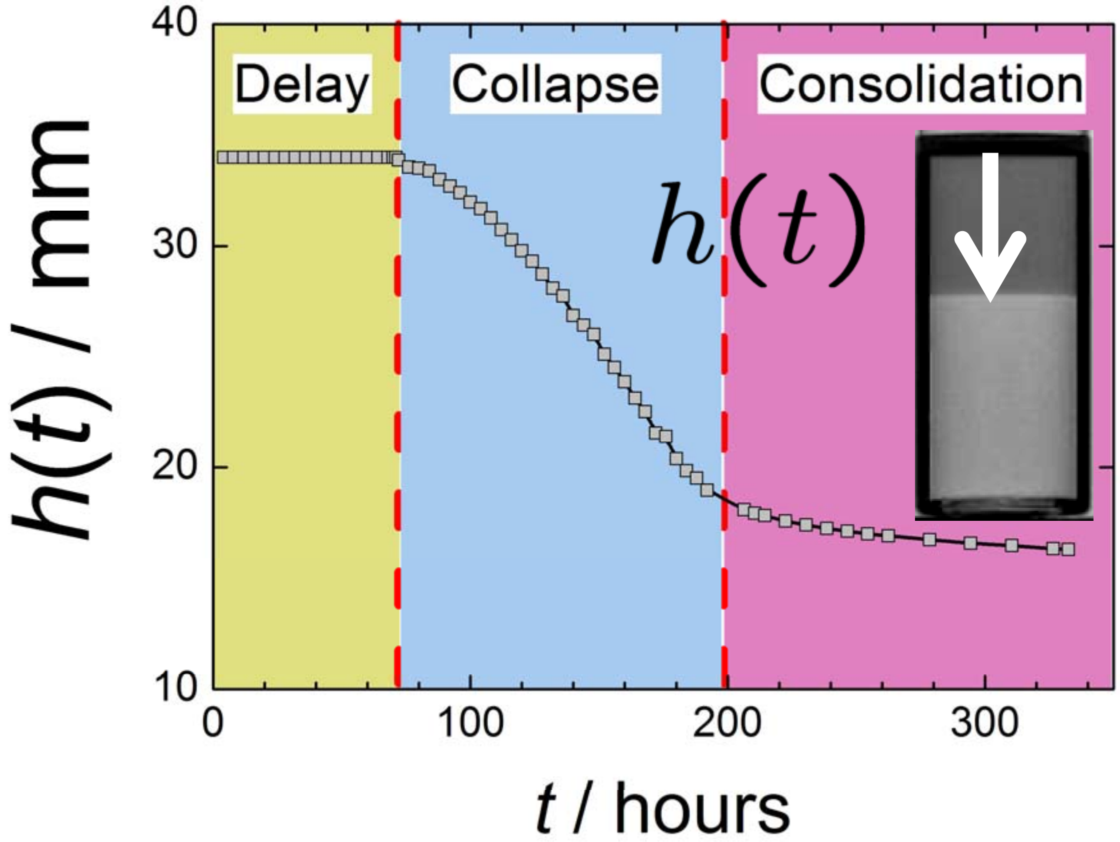
Time-lapse video microscopy

$c_P = 0.6 \text{ gL}^{-1}$ *X 7600 - 48 hours*



Time-lapse video microscopy



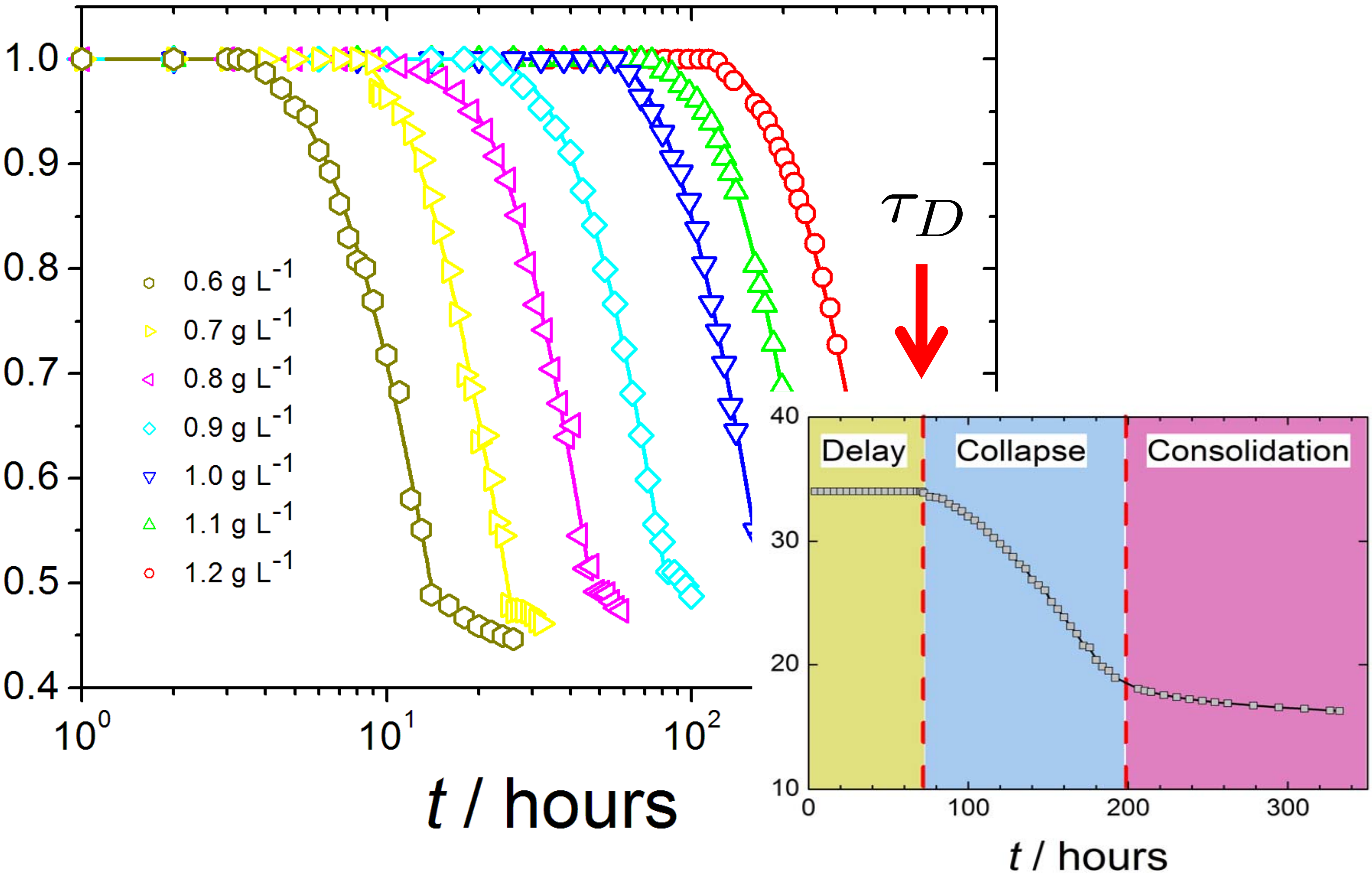


glass, d=23 mm, ϕ = 0.2, c_p = 1 g dm^{-3}

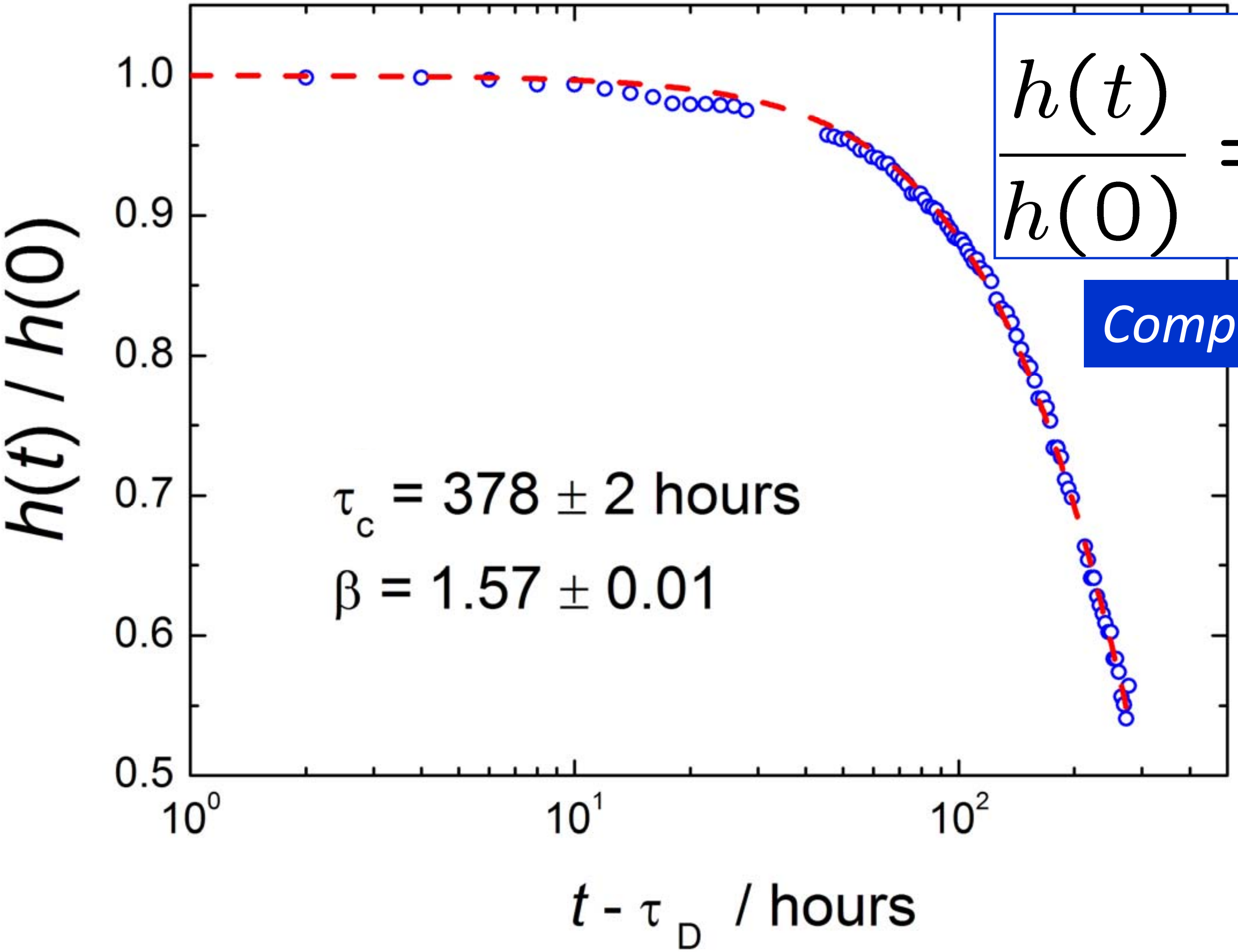
Accuracy: $\pm$ 0.25 mm

- Three-stage settling process
- Mechanism totally unknown

Vary initial height $h(0)$, [polymer], nature of walls



Time-dependent gel collapse



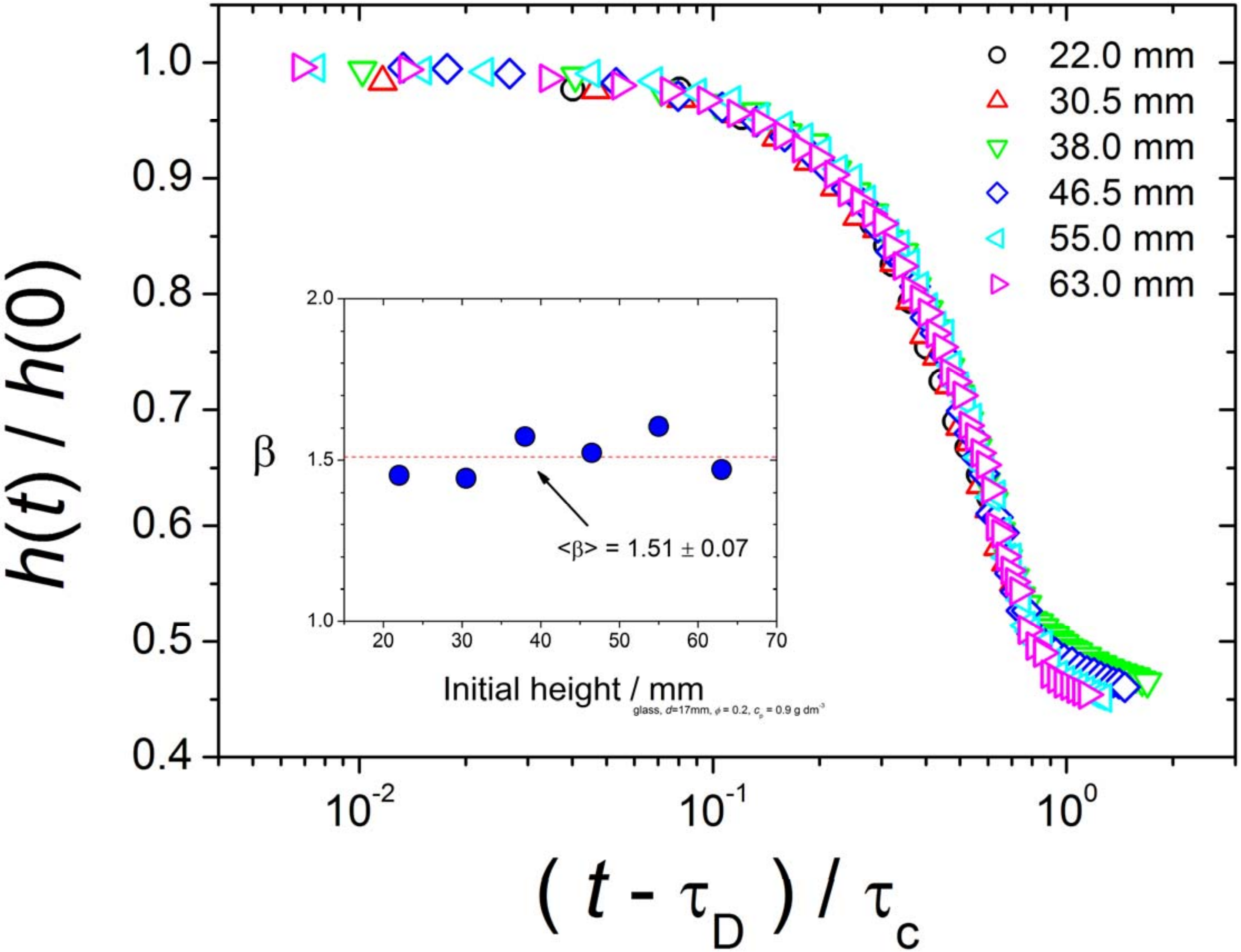
$$\frac{h(t)}{h(0)} = e^{-\left(\frac{t-\tau_D}{\tau_C}\right)^{\beta}}$$

Compressed exponential

glass, $h(0)$ = 39 mm, d=17mm, ϕ = 0.2, c_p = 1.2 g dm^{-3}

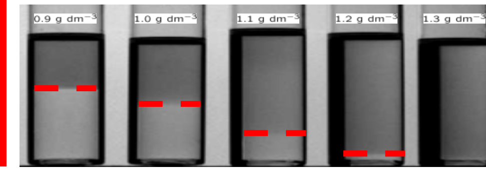
Height-independent scaling

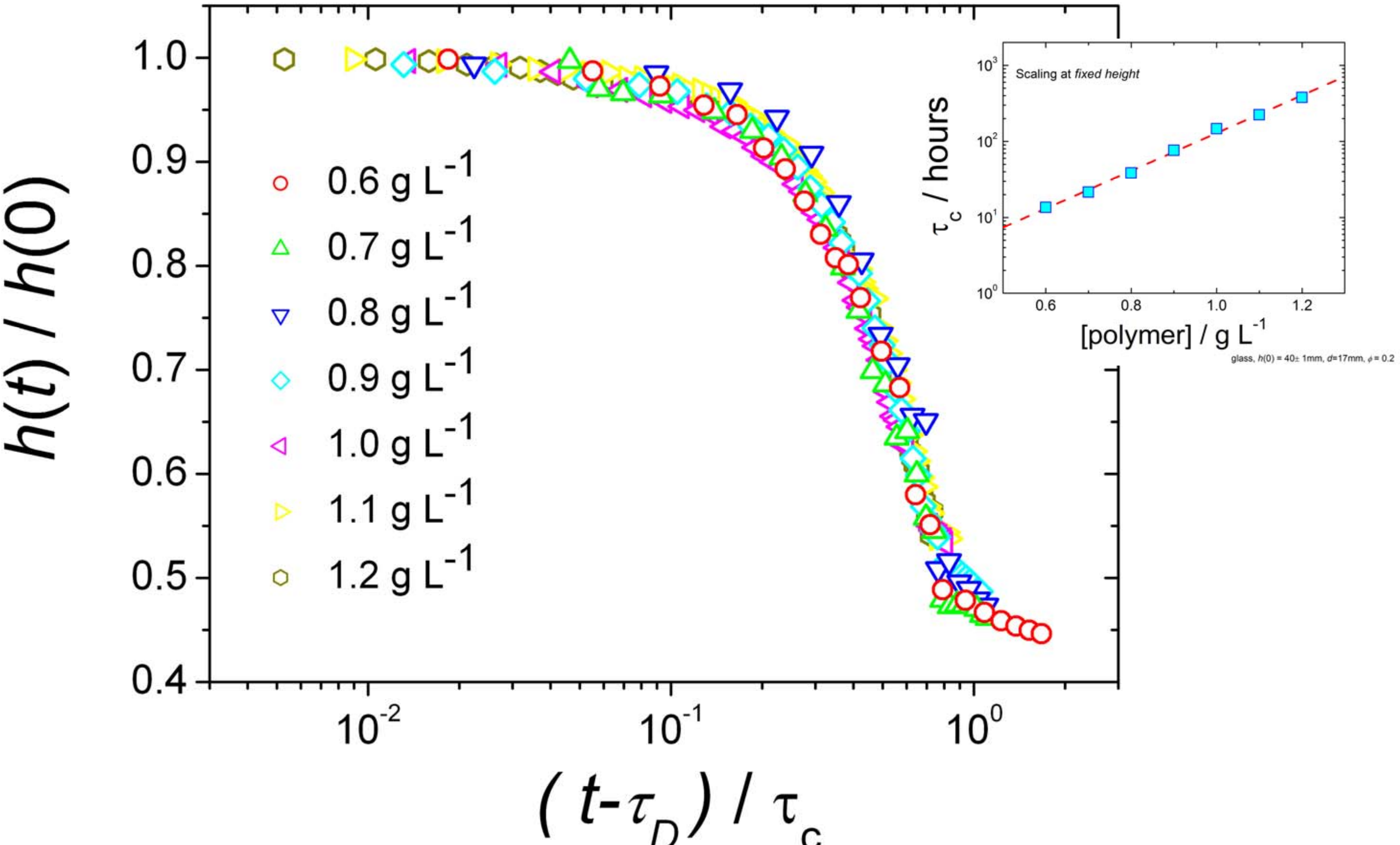
tall samples $h > w$



glass, d=17mm, $\phi = 0.2$, $c_D = 0.9$ g dm^{-3}

Universal time-dependent collapse

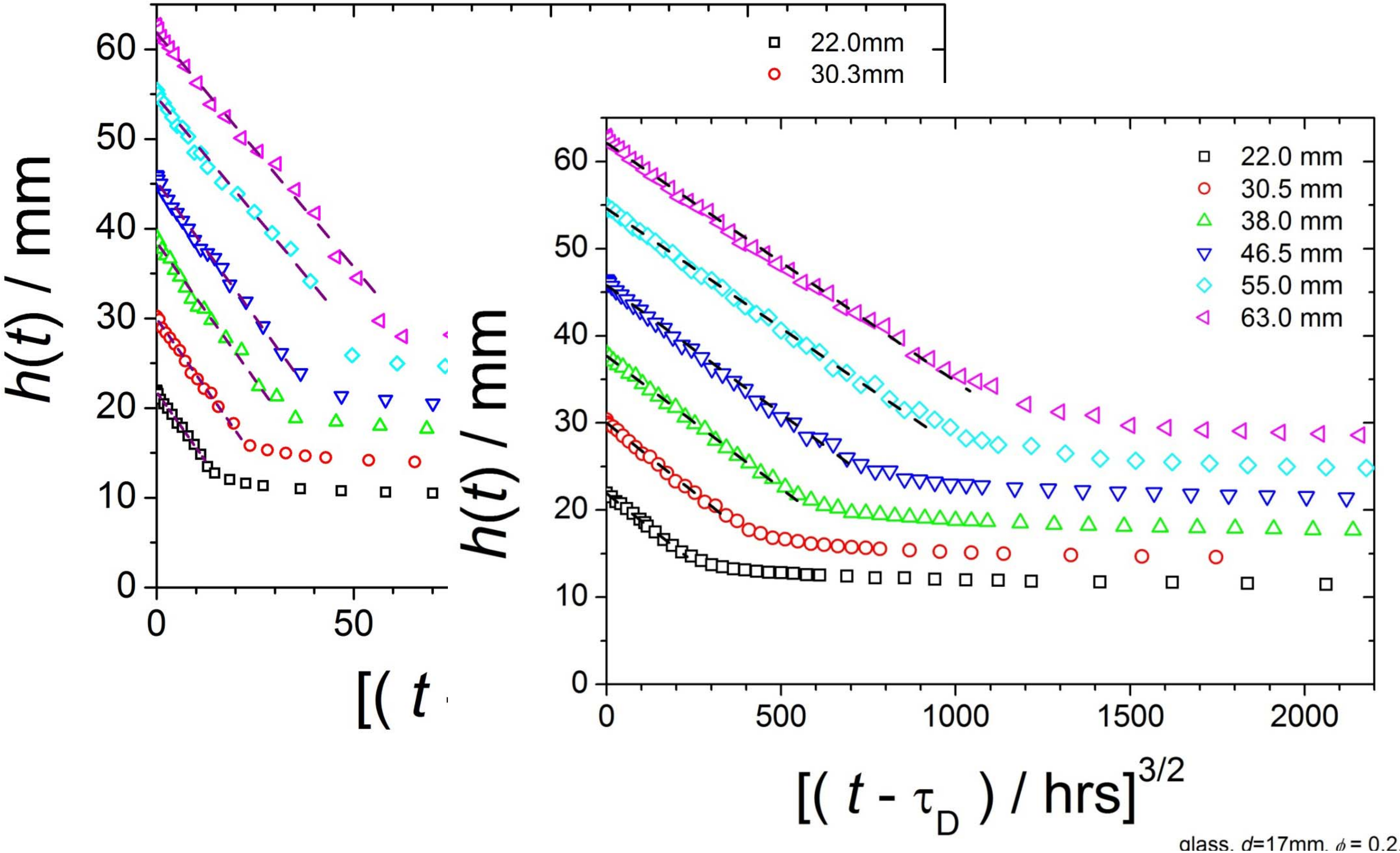


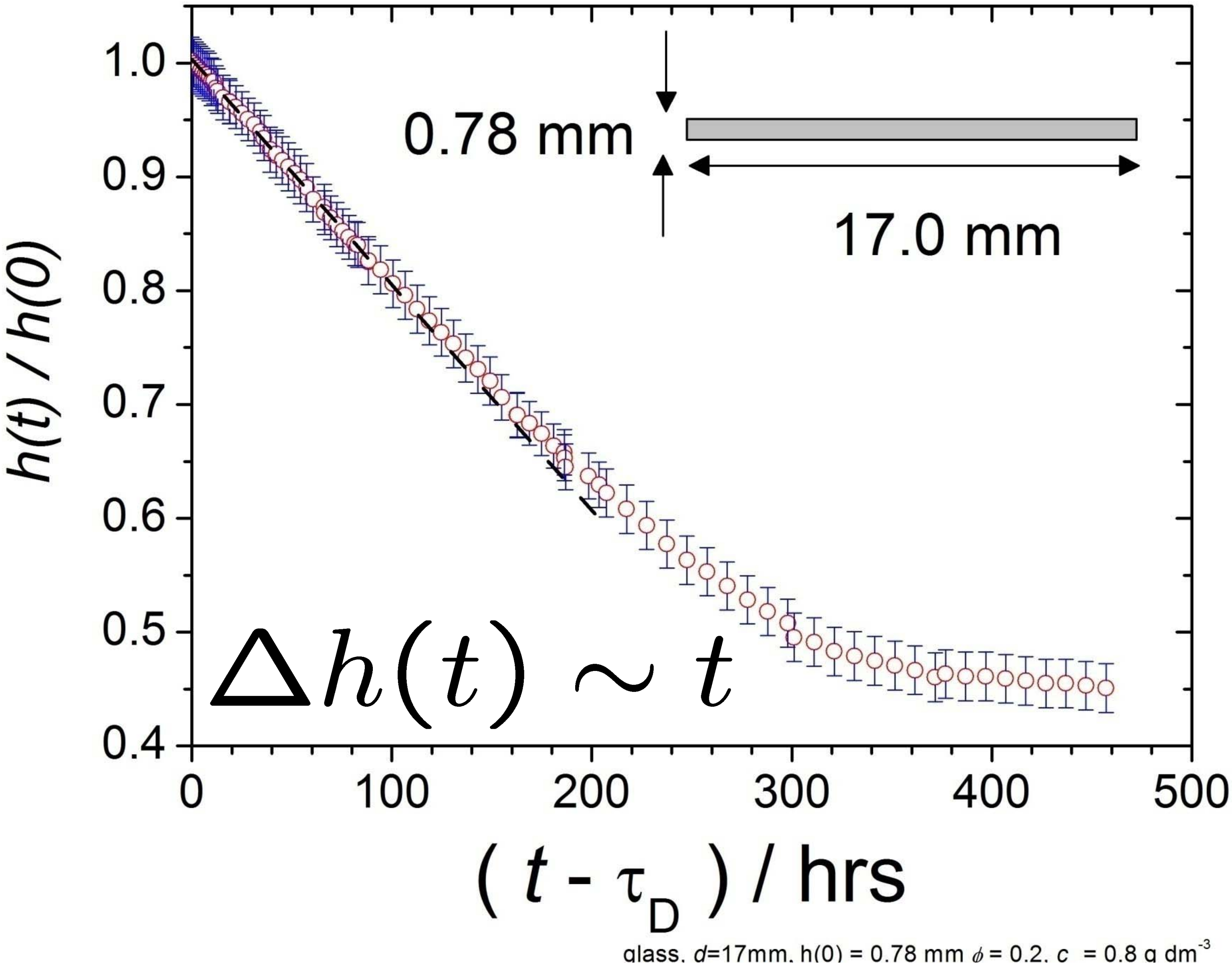


glass, $h(0)$ = 40± 1mm, d=17mm, ϕ = 0.2

Accelerated collapse

$$\Delta h(t) \sim t^{3/2}$$




1.0
0.9
0.8
0.7
0.6
0.5
0.4
0
100
200
300
400
500
h(t) / h(0)
(t - τ_D) / hrs
0.78 mm
17.0 mm
$\Delta h(t) \sim t$
glass, d=17mm, h(0) = 0.78 mm φ = 0.2, c = 0.8 g dm⁻³

Summary of key observations

Accelerated collapse

- Fast
- Tall samples

$$\Delta h(t) \sim t^{3/2}$$

Linear collapse

- Slow
- Short samples

$$\Delta h(t) \sim t$$

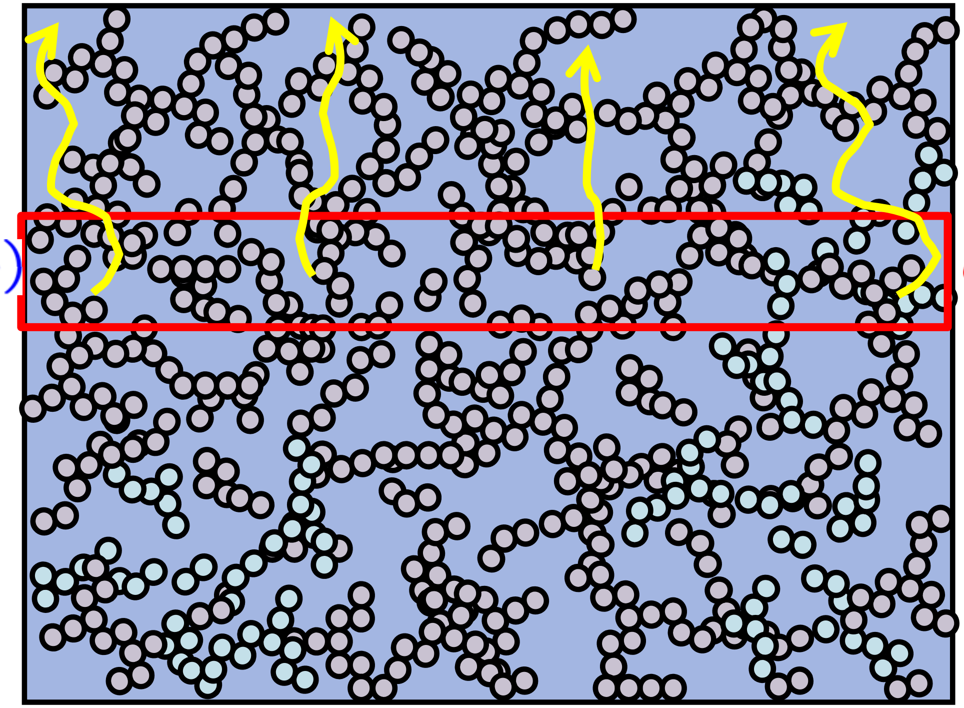
Origin of $t^{3/2}$ scaling

Gravitational collapse?

Darcy flow $\phi \partial_t u = k \partial_x p$

$\partial_x \sigma = -\Delta\rho g(1-\phi)$

Buoyancy stress



$\sigma = K\partial_x u - \phi p$

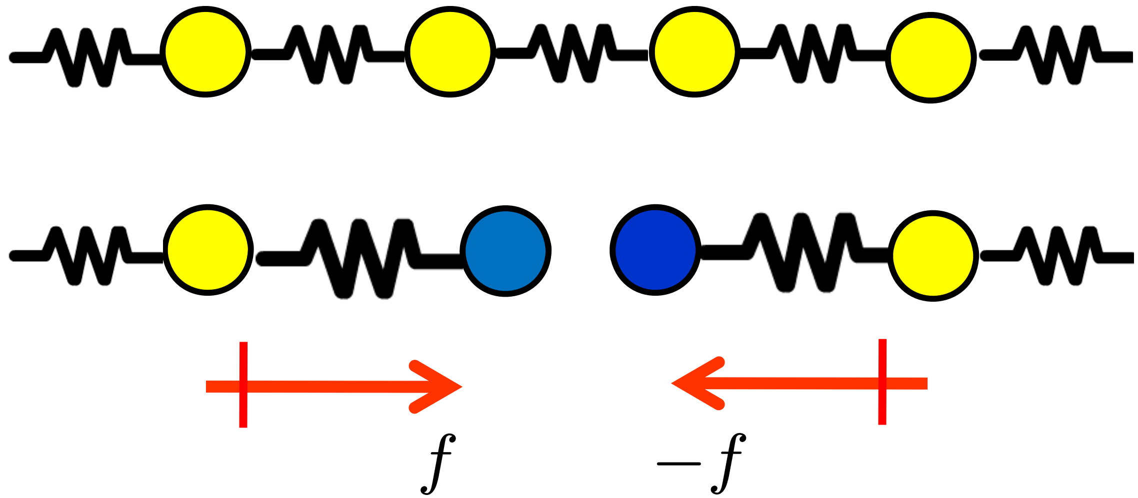
Elastic stress

$$\Delta h(t) \sim \left(\frac{\pi^2 \Delta\rho g(1-\phi)k}{8\phi} \right) t$$

- *Linear collapse*

Origin of $t^{3/2}$ scaling — Stress dipoles

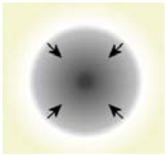
Aging of gel



$t < t'$

$t \geq t'$

Micro-collapse

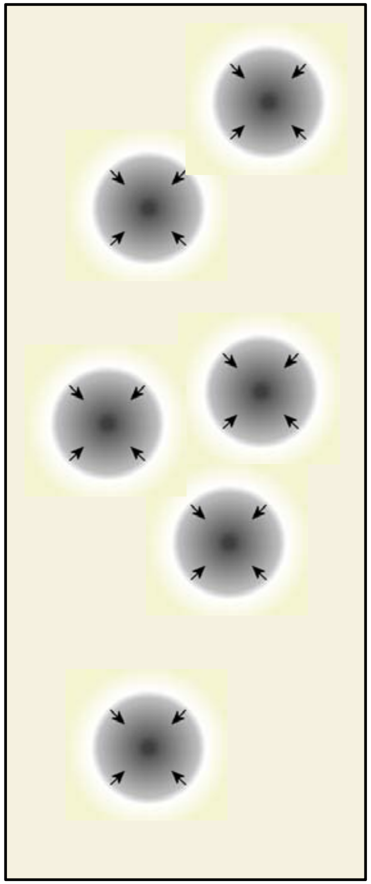


Point dipole of intensity Q(t)

Assume dipole intensity is approximately linear in time

$$Q(t) = Q_0(t - t')/\theta$$

Cipelletti et al. Phys. Rev. Lett. 84, 2275, (2000)



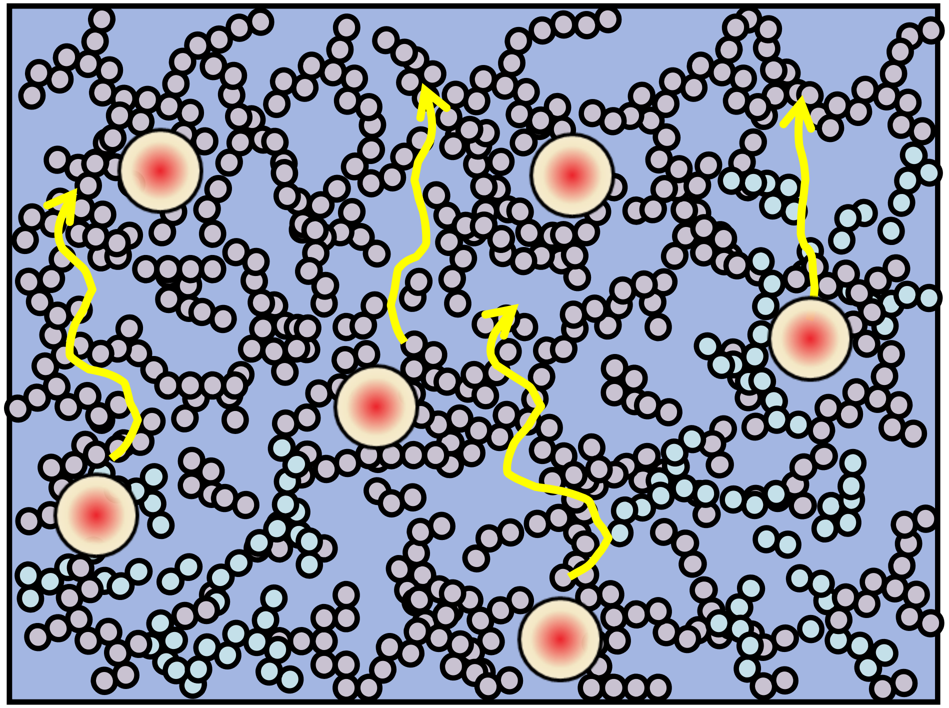
Elastic gel

Gel shrinkage:

$$\Delta h(t) \sim t$$

What is missing?

Poroelasticity of gel



Fluid-filled elastic matrix

Propagation of stress by diffusion

$$\partial_{xx}u - \frac{1}{D_s}\partial_t u = -\frac{1}{K}f$$

Stress diffusion constant determined by elastic and hydraulic properties of network

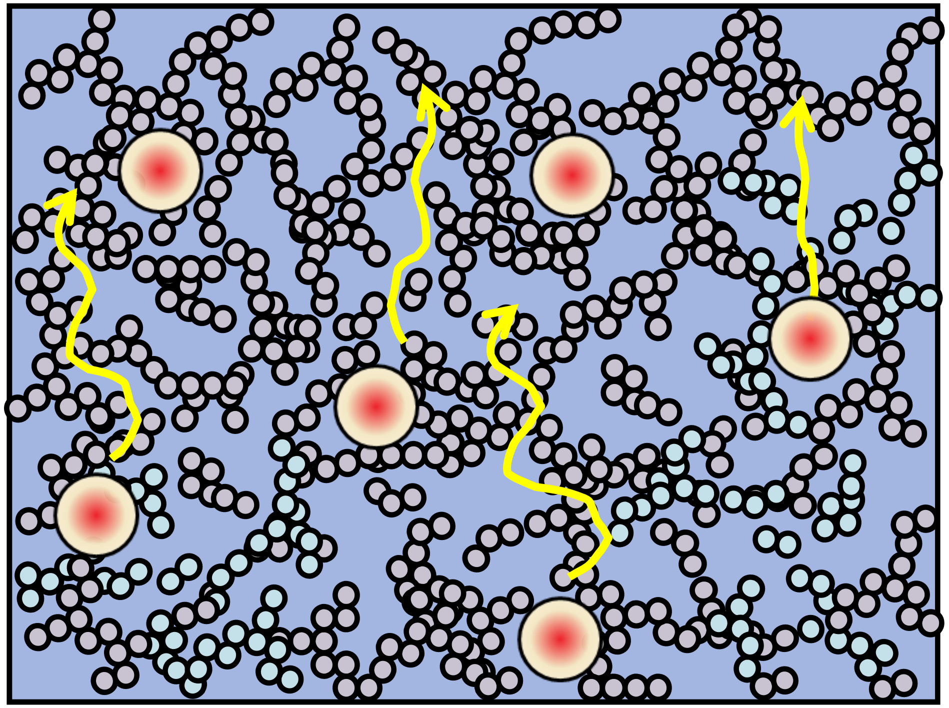
$$D = \frac{kK}{\phi}$$

For current gels estimate $D \sim 10^{-10}\mathrm{m}^2\mathrm{s}^{-1}$

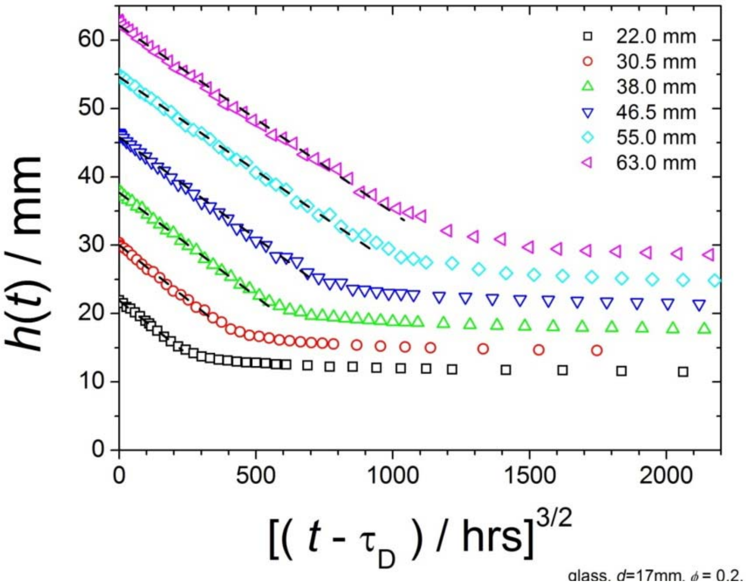
Equilibration of stress over 10 mm take about 70 hours

Origin of $t^{3/2}$ scaling

Stress diffusion in gels



Fluid-filled elastic matrix



$$\lim_{t\to 0}\{h(0)-h(t)\} = \frac{\rho\phi_0}{\pi^{1/2}D^{1/2}K\theta}t^{3/2} = At^{3/2}$$

Conclusions

- Novel mechanism of collapse in weak gels
- Internal stress inhomogeneites lead to accelerated collapse of gels
- At small heights switch in mechanism to conventional linear collapse

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