Aging in laponite – water suspensions.

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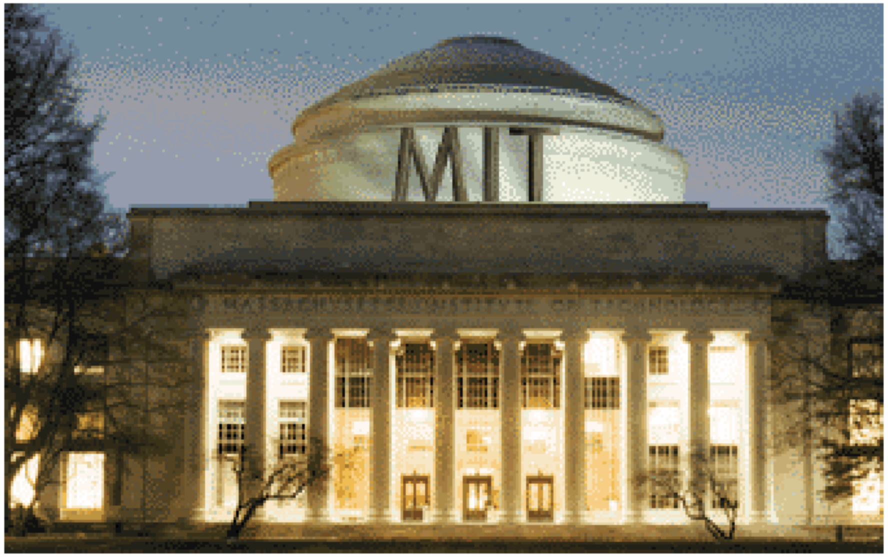
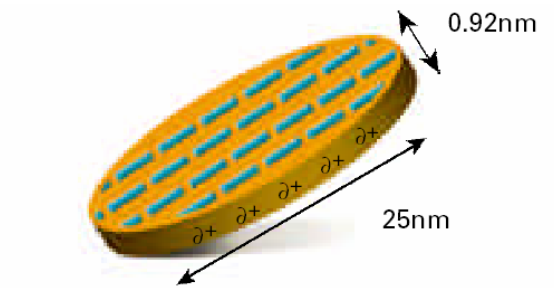


Outline

- Laponite
  - Basic background.
- Laponite in suspension
  - *Bonn et al., Langmuir* (1999)**, 15***,* 7534
  - A glass or a gel?
- Aging Laponite in suspension
  - Bellour *et al., Phys. Rev E* (2003) **67**, 031405
  - Investigates spatial dependence of dynamical behaviour.
- Rheology of laponite suspensions
  - *Bonn et al., Europhys. Lett.*, (2002) **59,** 786
  - Compare with predictions of the SGR model

Laponite



- When suspended in an aqueous solution the face of the laponite is charged negatively.
- Depending on the pH of the solution the sides can be charged positively.
- “House of cards” structure of laponite has been proposed since the faces and the sides can have electrostatic attraction.
- Computer simulations show that such “house of cards” structures are possible.
- A “fractal network” has been proposed in some works.
- Electron Microscope images show particles are isolated and hardly touch.

So, do laponite-water suspension have any structure?

Glass & Gel: Major Issues

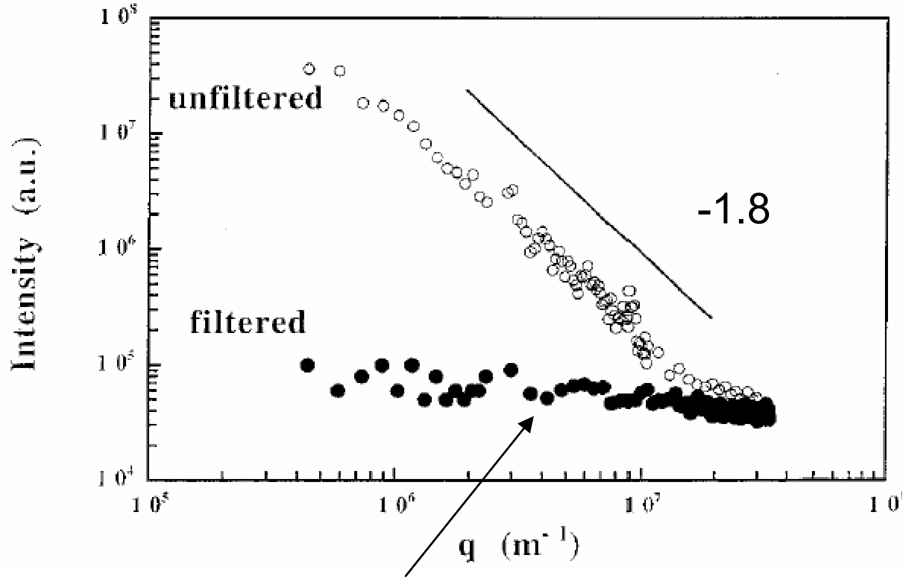
Bonn *et al*. (1999) Langmuir, 15, 7534

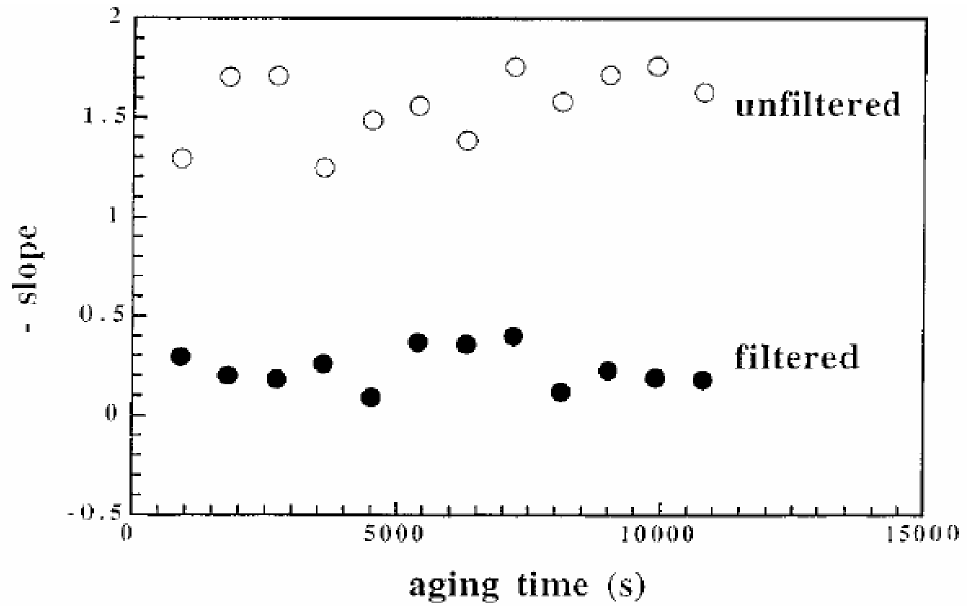
- Gel => Comparatively Low volume fraction of solid with network. Network can be fractal.
- Glass => High volume fraction of particles with no network present.

- Intensity of scattered light varies with the wave vector as a power law with a negative exponent that characterises the fractal dimension =>signature of fractal networks.
- Power law behaviour of the intensity Vs the wave vector is observed in experiments in laponite dispersions.
- Laponite dispersions (in water) generally considered gels.
- Rheological properties are usually related to the existence of a fractal structure.

However reports exist where NO strong dependence of scattered intensity Vs wave vector is evident.

Results: SLS



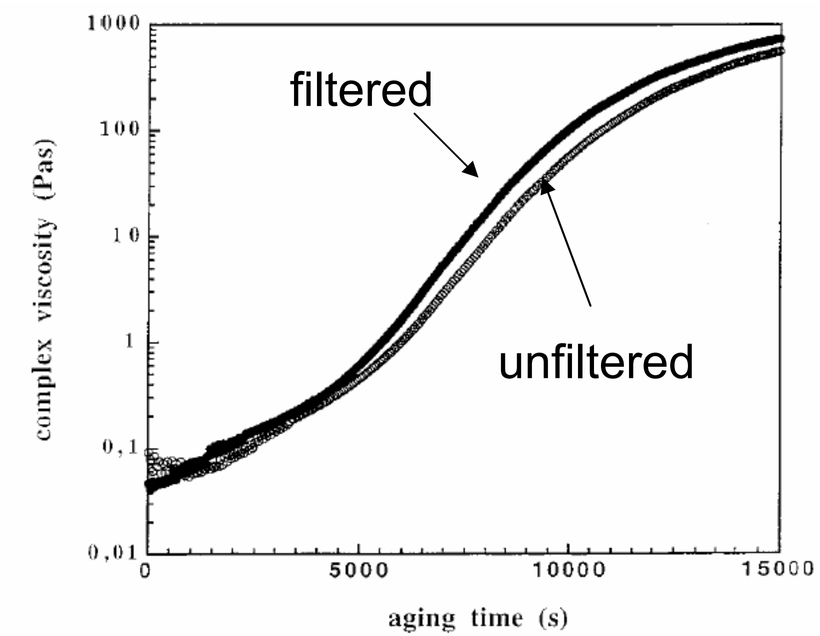


Intensity independent of wave vector => no structure in the sample!!

- Slope of -1.8 present immediately after sample preparation. Slope should be zero at the beginning as no network has yet formed!!
- Slope does not change during aging for either samples.

Observed fractal structure is an artifact resulting from incomplete dissolution of laponite.

Results: Rheology



- Effective volume occupied by particle is much larger particle volume. Discs can rotate.
- Particles are charged, and the screening length of electrostatic interaction can be high.
- When the above two effects are considered the dynamics can be related to those in colloidal glass.

- Viscosity changes by 4 orders of magnitude over 15000 s aging time.
- Insignificant difference between the filtered and un-filtered samples.
- Viscoelasticity is not caused due to fractal network.
- So why does the viscosity increase?

Comments

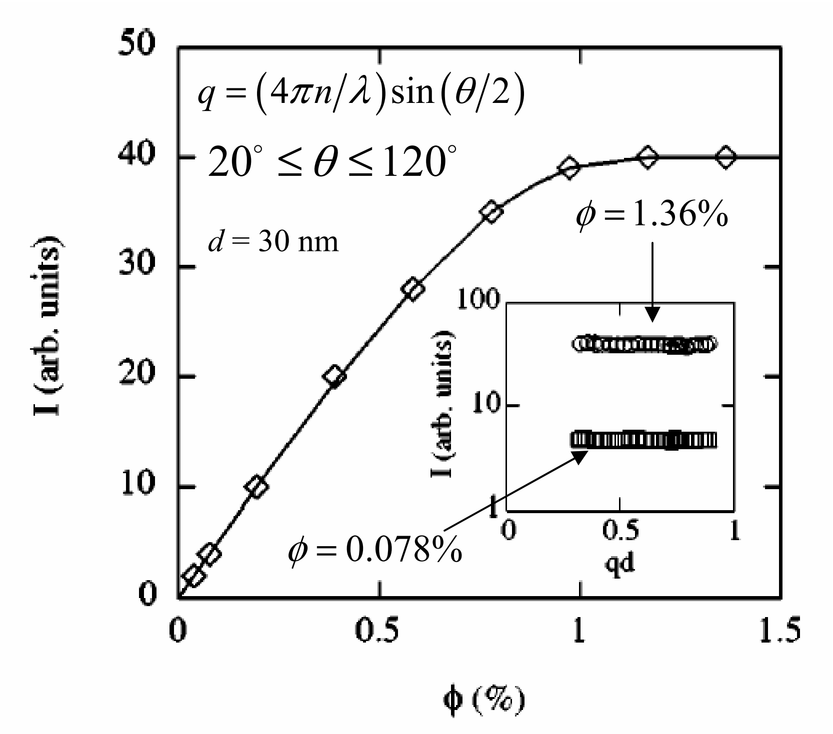
- Difference between (soft) glass and gel is difficult to quantify experimentally.
- Rheologically, both a glass and a gel have a yield stress (at least an apparent one). Plus both become viscoelastic after quench into a glassy, or gel phase.
- Existence of a network structure might be the only difference… but this cannot be always established easily experimentally.

Aging processes in soft glassy colloidal suspensions

Bellour *et al*. (2003) Phys. Rev E, **67**, 031405

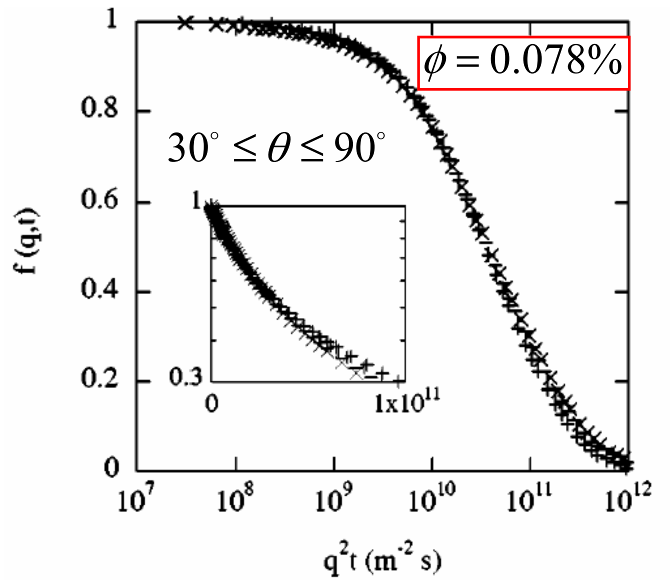
- Investigates dynamical behaviour in laponite suspensions.
- Uses static and dynamic light scattering.
- Also uses “Multi speckle” technique to study slower dynamics.

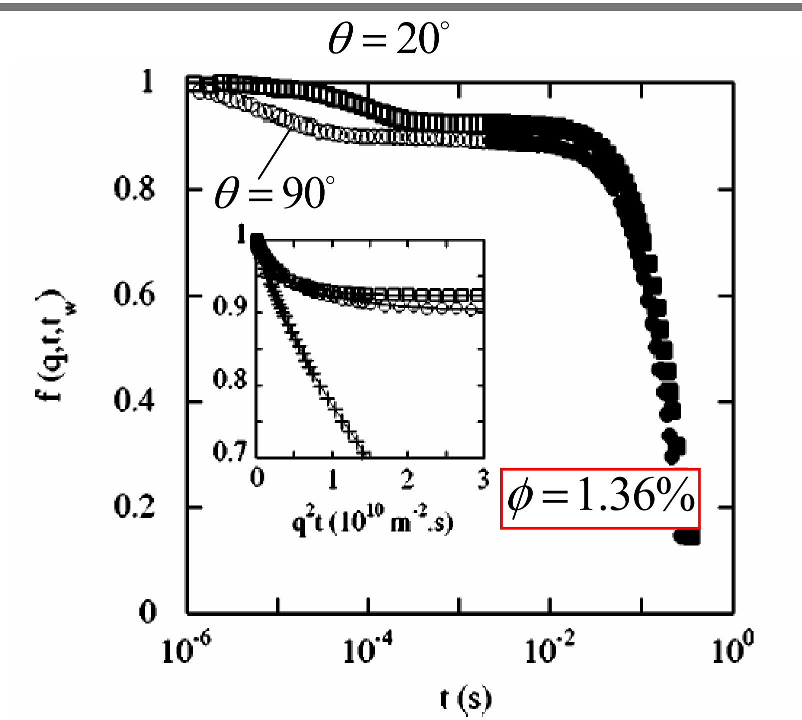
Static Light Scattering results



- Weak ϕ dependence of I at large ϕ.
- I decreases with increasing ϕ in the vicinity of ϕ^*. $(\phi^* \simeq 0.7\%)$
- I proportional to ϕ for $0.7\% \le \phi \le 0.1\%$
- Total intensity of scattered light independent of q (inset) - indicates spatially homogeneous samples with a disordered arrangement.

Fast relaxation





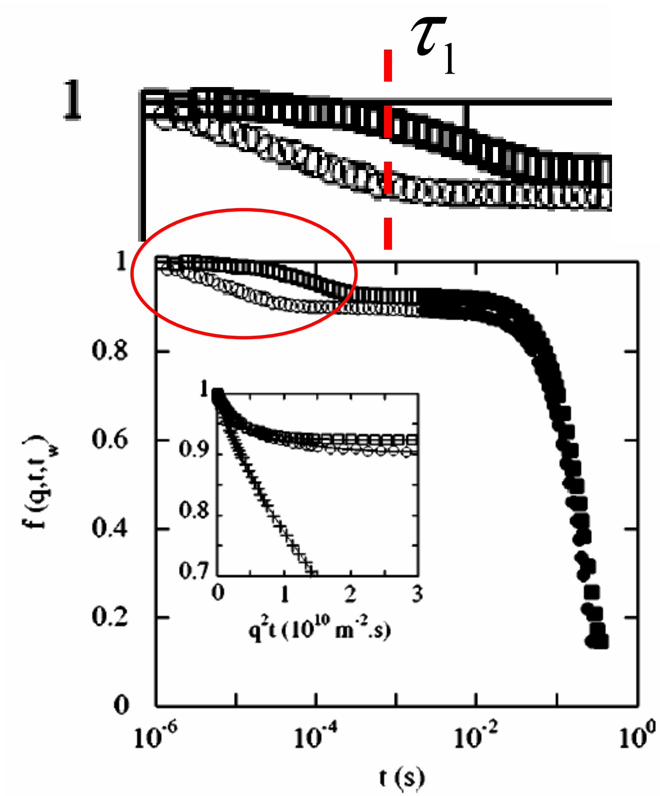
$\phi < \phi^*$ $\quad (\phi^* \simeq 0.7\%)$

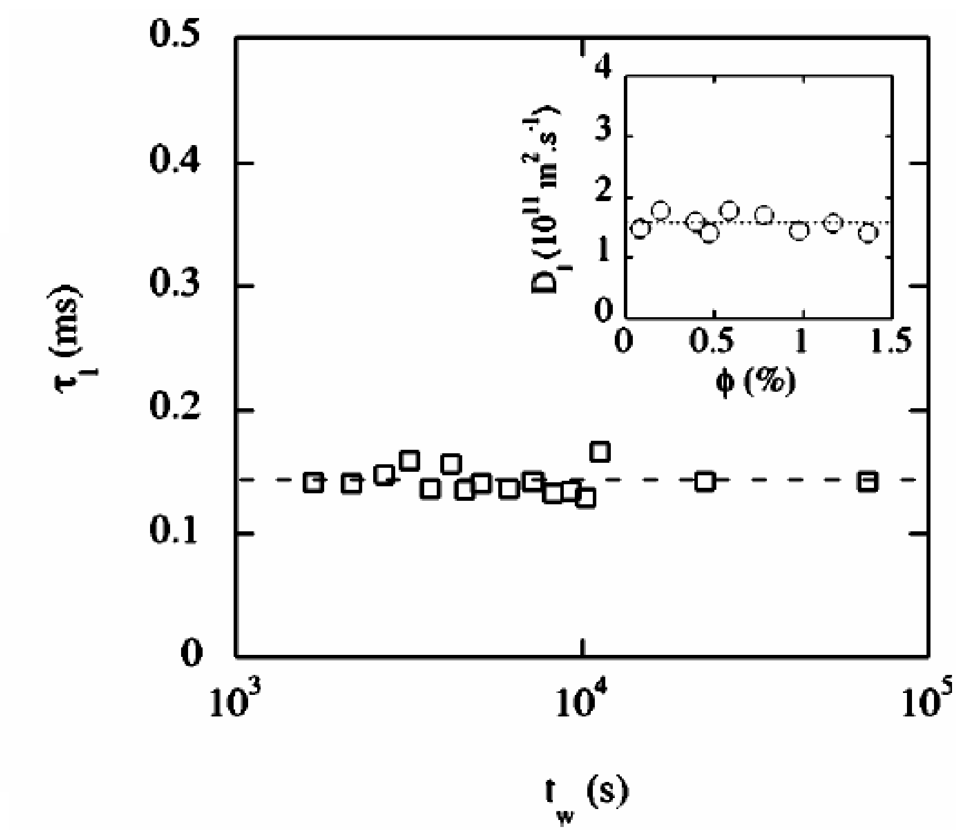
- Diffusive. $S(q,t) = \exp(-2Dq^2t)$
- Not quite a single exponential.
- Repulsive interaction between particles presumed to have a role in this.

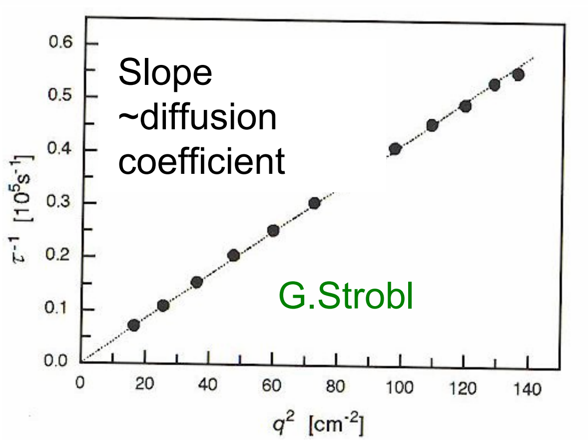
$\Phi > \Phi^*$: Two stage relaxation

- Fast (diffusive) relaxation in the time scale τ_1.
- Amplitude of fast relaxation decreases with f.
- Slow relaxation at longer time.
- Slow relaxation process is time dependent.

Fast relaxation (contd)

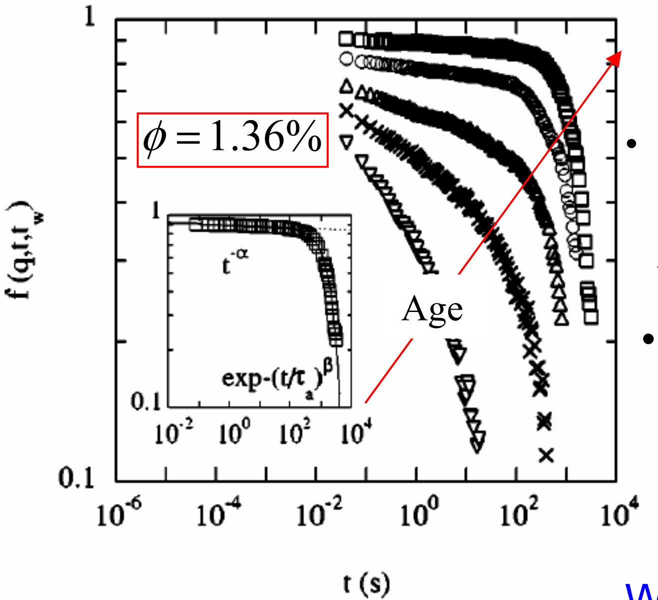






- Relaxation time (τ_1) does not depend on the state (liquid / glass), or on the age of the sample.
- *Unique* diffusion coefficient over all concentration ranges.

Slow relaxation

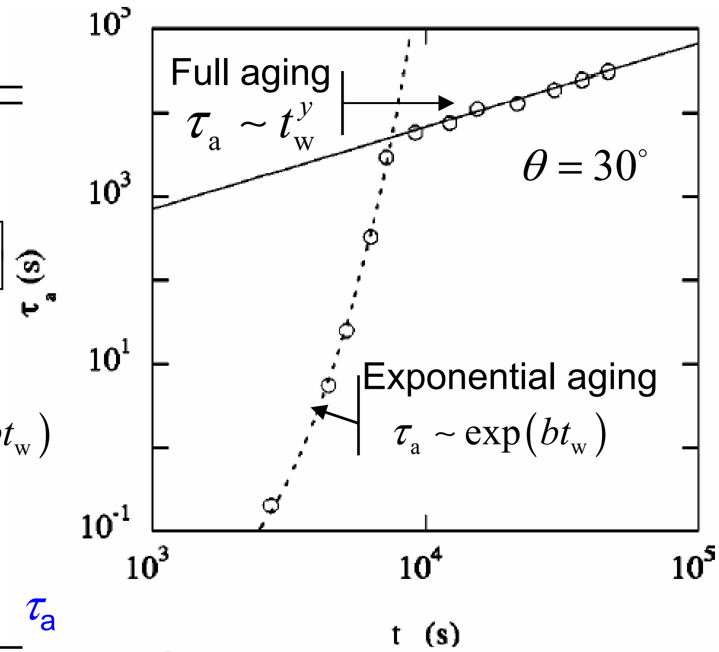


Aging of the relaxation time

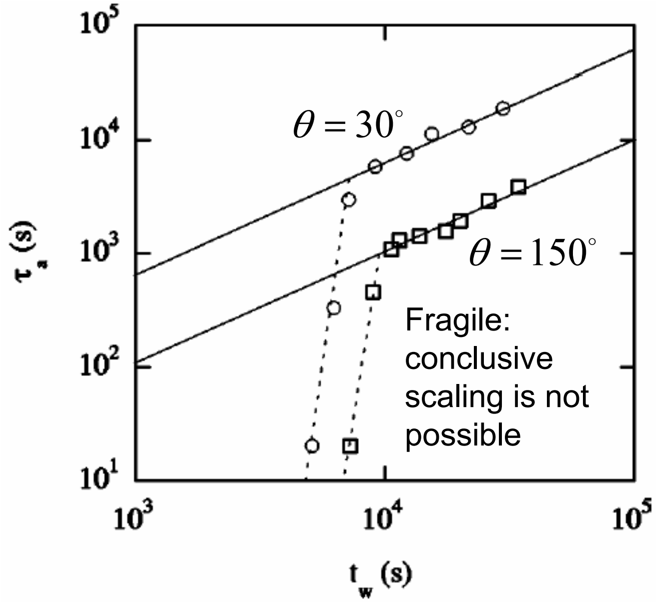
- Fit stretched exponential to the data.

$$f(q,t,t_w) = at^{-\alpha}\exp\left[-(t/\tau_a)^{\beta}\right]$$

- Two regimes.
  - Exponential: $\tau_a \sim \exp(bt_w)$
  - Full-aging: $\tau_a \sim t_w^{y}$



Wave vector dependence of τ_a

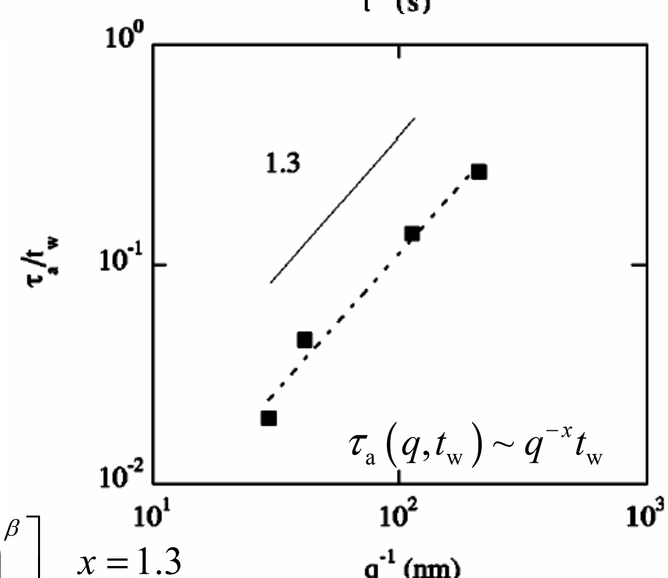


- In the exponential region, the fast and the slow relaxation is not well separated in time.
- Scaling established in the full-aging region only.

$$\tau_a(q,t_w) \sim q^{-x}t_w$$

- In Full-aging regime the dynamic structure factor has form

$$f(q,t,t_w) = \exp\left[-m\left(q^{x}\frac{t}{t_w}\right)^{\beta}\right]$$



$x = 1.3$

$\beta = 1.35$

Comparison with SGR Model: LVE

Bonn et al., Europhys. Lett., (2002) **59,** 786

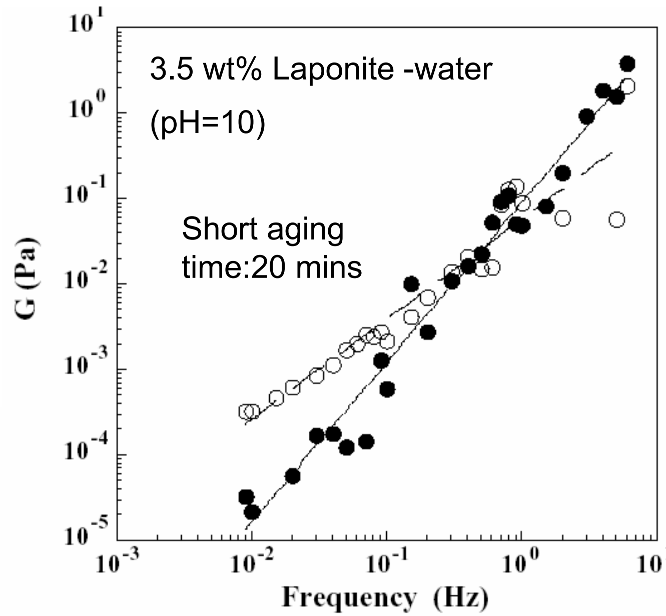
Model LVE predictions

$$G' \propto \omega^2 \quad (x > 3)$$

$$G' \propto \omega^{x-1} \quad (1 < x < 3)$$

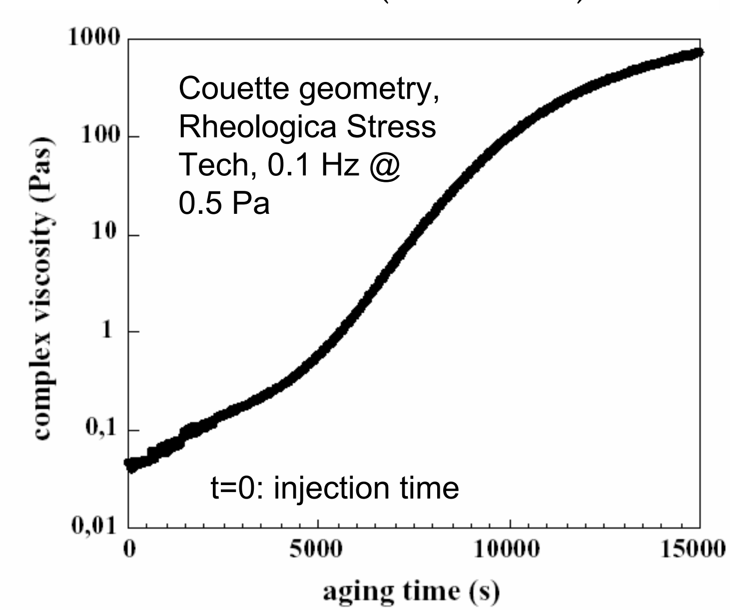
$$G'' \propto \omega \quad (x > 2)$$

$$G'' \propto \omega^{x-1} \quad (1 < x < 2)$$

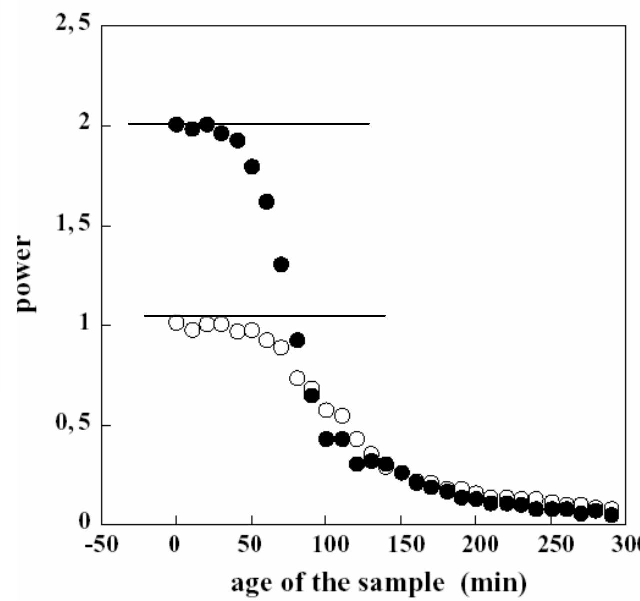


- Maxwellian behaviour observed at short aging times.

Qualitatively correct



- Complex viscosity increases 4 orders of magnitude in 15000s (~ 4 something hours).

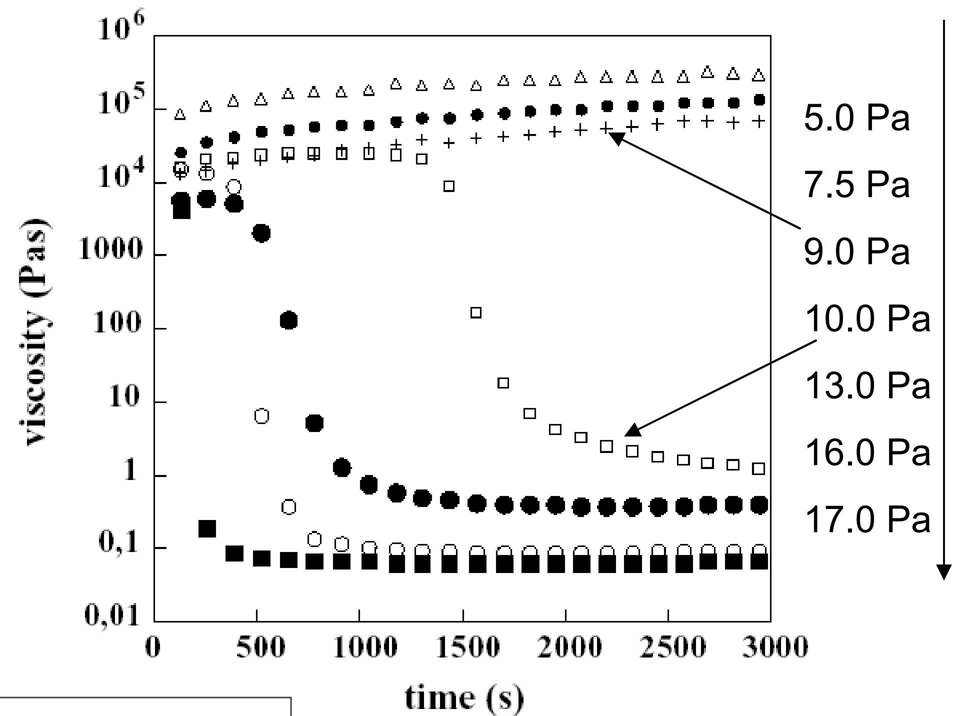


- At longer times the frequency dependence changes rapidly, approaching independence at long times.
- Calculated value of x=1.1

Comparison with SGR model: Shear

Observations in Creep Experiments

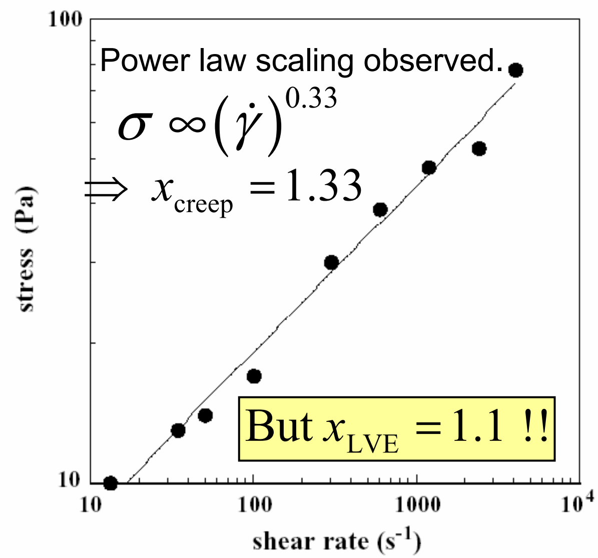
- Below certain critical values of stress viscosity increases indefinitely.
- For stresses larger than the critical value, viscosity decreases t reach a low steady state value after a long time.
- Bifurcation occurs at critical stress: fluid either stops flowing, or it fluidizes.
- Aging and “Rejuvenation” due to “de-structuring” compete to establish dynamical response



Model Predictions

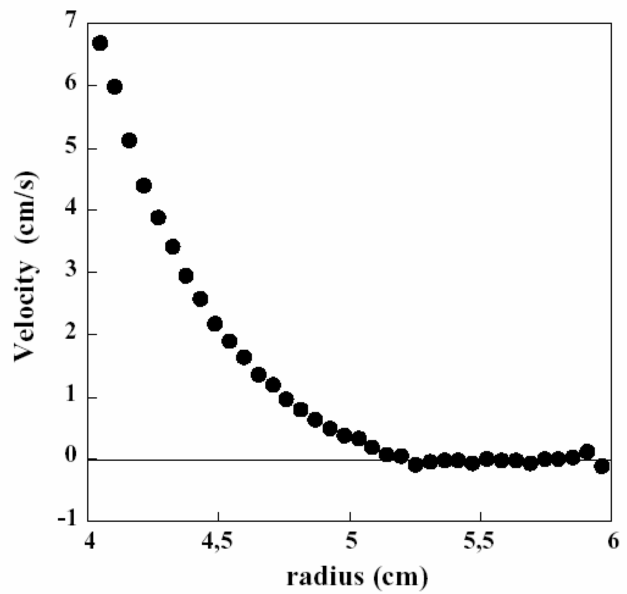
$$\sigma \propto \dot{\gamma}^{x-1} \quad (1 < x < 2)$$

$$\sigma = \sigma_y \quad (x \leq 1)$$



Depending on the value of applied stress x changes : it is not a property of the system, but depends on the way it is forced.

Existence of sheared and un-sheared zones



Observations in Couette Flow

- MRI measurements on Couette flow set-up (very clever – I think)
- Two regions; one with shear, and other without any apparent shear is observed.
- Limits are situated at a critical radius r_c.
- In the sheared zone. $\sigma \propto (\dot{\gamma})^{0.24}$
- In the un-sheared zone the viscosity is infinite.

- *Two different values of the "effective temperature" (χ) can exist in the same system at the same time.*
- *The observed coexistence of a sheared and an un-sheared part of the material is likely to be a general property of these soft glassy materials.*

Conclusions

- Dynamics of laponite suspensions above the critical volume fraction can be considered in terms of colloidal soft glass.
- The aging behaviour of the relaxation time of these suspensions show two distinct regimes: an exponential regime, and a linear regime.
- The SGR model can predict the rheology of these suspensions qualitatively. Some concerns regarding the nature of the “effective temperature” remain.
- Experiments confirm the existence of a sheared and a infinite viscosity region within the material in simple Couette flows. The SGR model does not predict this.