Cement paste rheology and microstructure

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ADVANCED CHEMICALS

open questions

- what is the origin of cohesion of cement paste?
- what are the phenomena which cause setting (stiffening)?
  - ✓ precipitation of hydrates?
  - ✓ growth of CSH nuclei?
  - ✓ aging?
- what causes the differences in paste rheology with different admixtures?
- how can we control
  - ✓ hydration rates?
  - ✓ microstructure?
  - ✓ mechanical properties?

origin of cohesion

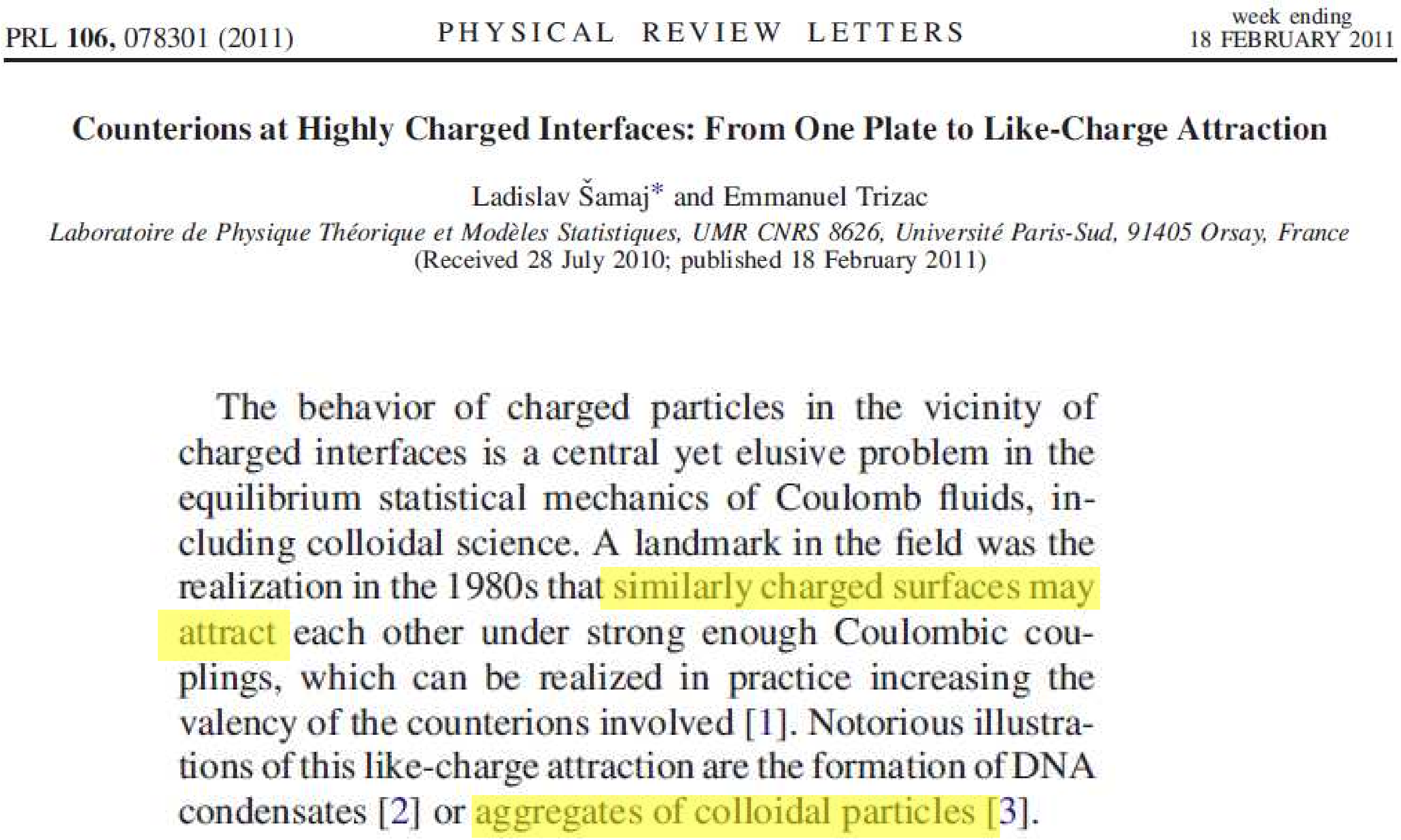
C3S and C-S-H in suspension: at high pH ≈ 13 the silanol surface groups will hydrolyze:

$$-\mathrm{SiOH} + \mathrm{OH}^- \rightarrow -\mathrm{SiO}^- + \mathrm{H_2O}$$

the surfaces will be negative with high charge density:

$\sigma \approx 0{,}8$ C/m2 at pH 14
$\sigma \approx 0{,}2 \div 0{,}4$ C/m2 at pH 12

why can surfaces with like charges attract?



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Counterions at Highly Charged Interfaces: From One Plate to Like-Charge Attraction

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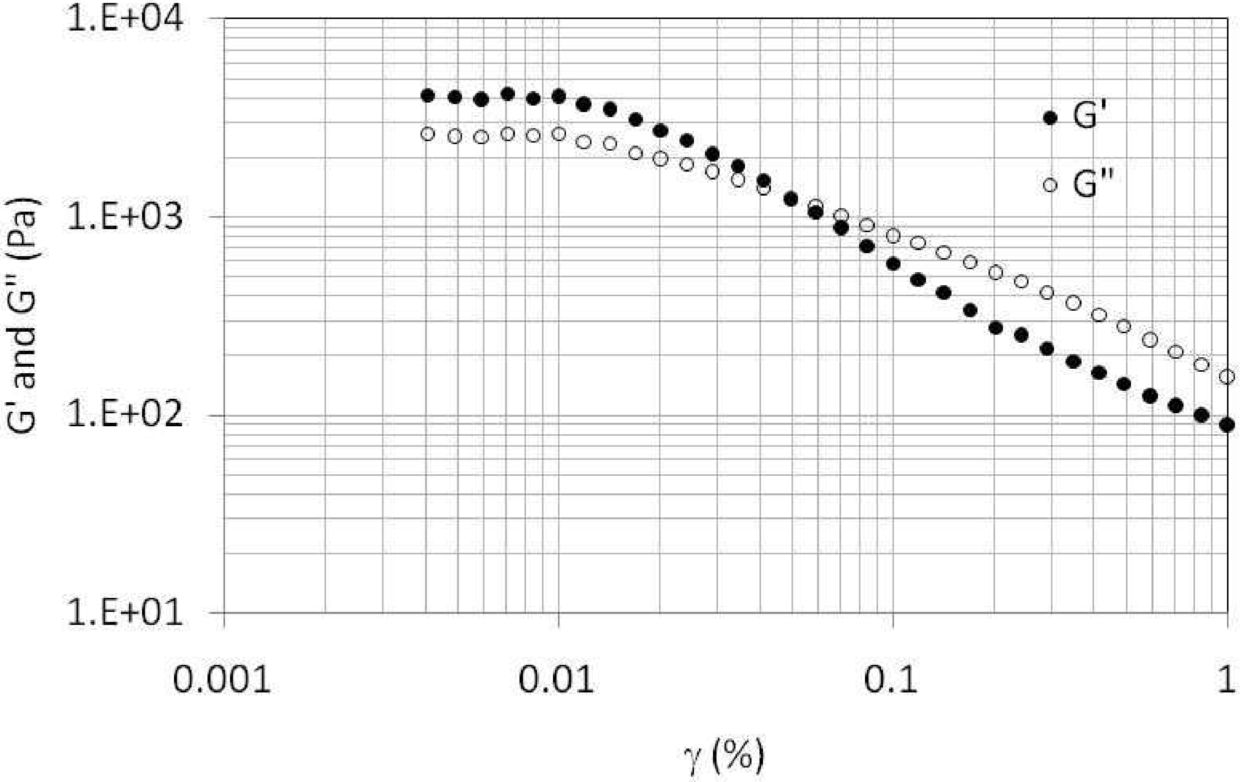
The behavior of charged particles in the vicinity of charged interfaces is a central yet elusive problem in the equilibrium statistical mechanics of Coulomb fluids, including colloidal science. A landmark in the field was the realization in the 1980s that similarly charged surfaces may attract each other under strong enough Coulombic couplings, which can be realized in practice increasing the valency of the counterions involved [1]. Notorious illustrations of this like-charge attraction are the formation of DNA condensates [2] or aggregates of colloidal particles [3].

correlation forces

experimentally

cement paste is an attractive colloid

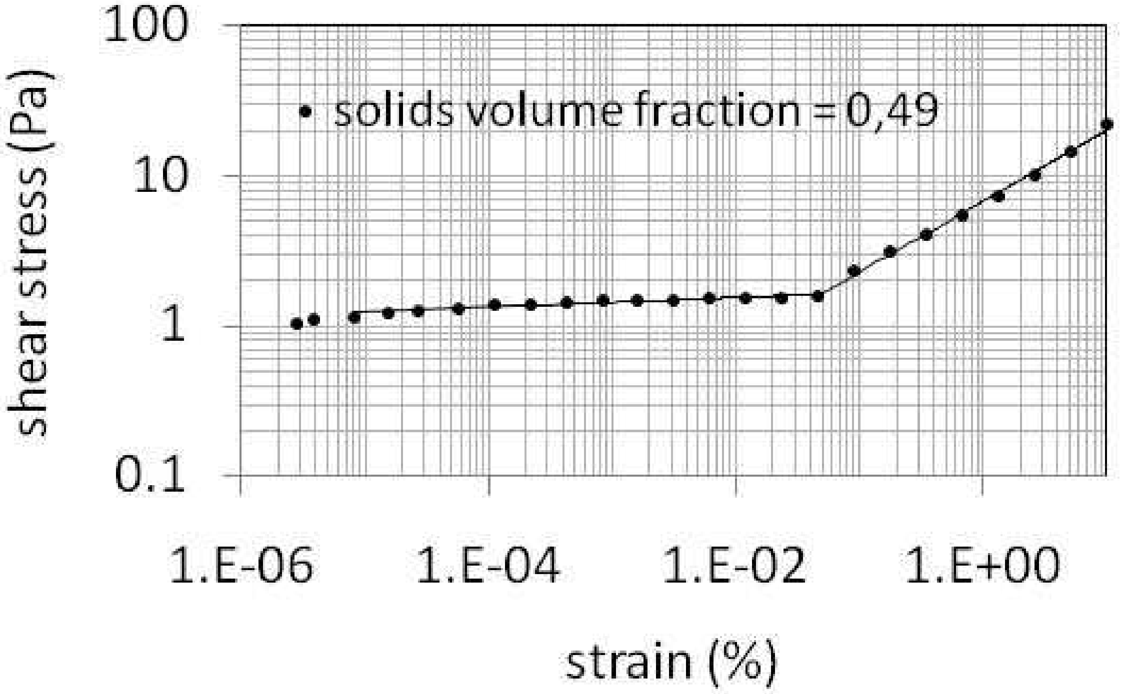


w/c = 0,5
Φ = 0,39

just after mixing: the paste is elastic and yields for large enough strains

experimentally

cement paste is an attractive colloid

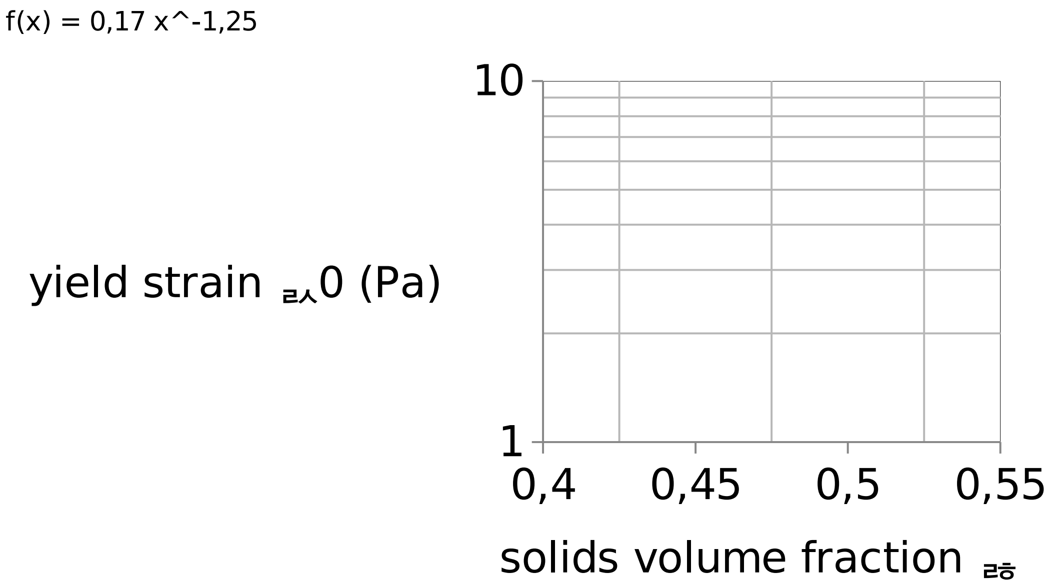


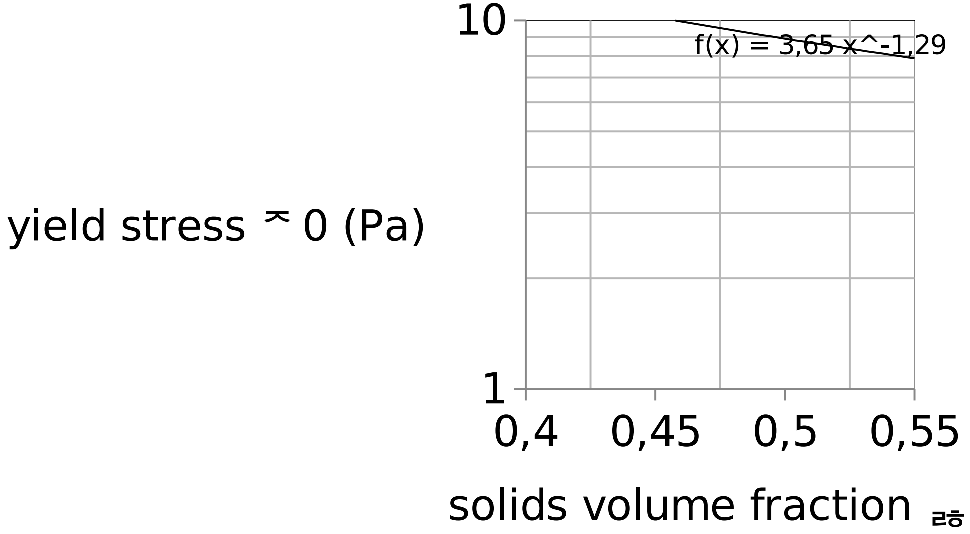
yield stress can be measured also with a continuous deformation: yield stress is equal, yield strain is larger

flow start-up is dilatant

just after mixing: the paste is elastic and yields for large enough strains

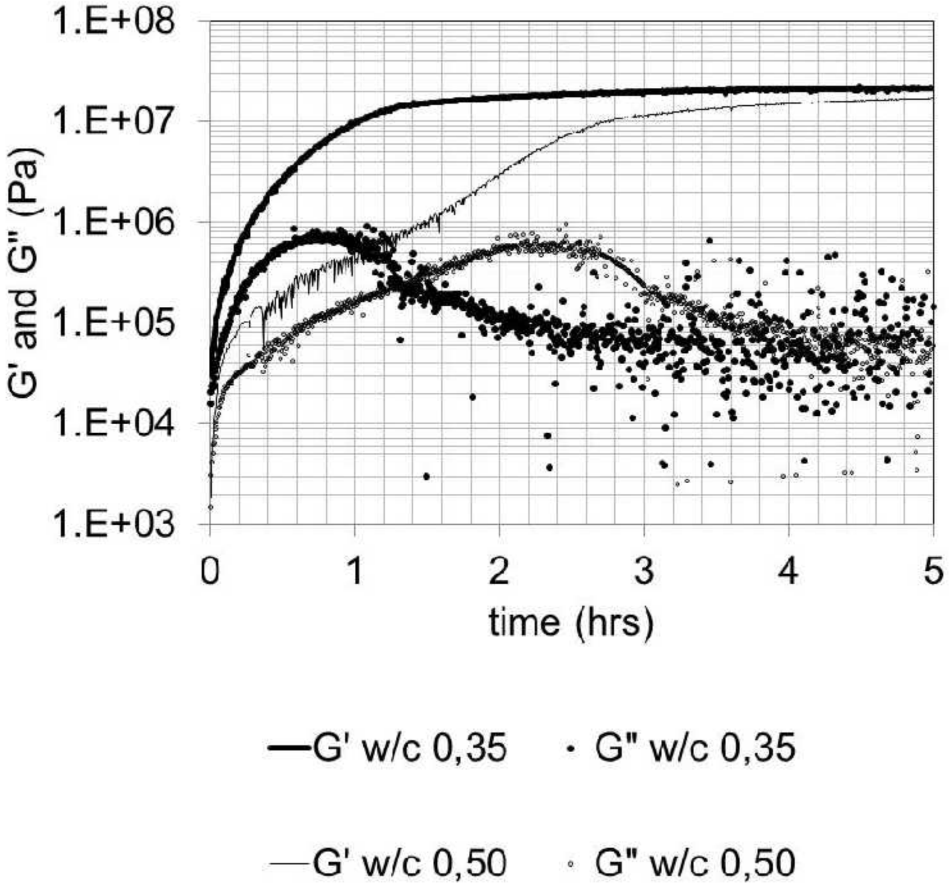
yield stress and yield strain exhibit exponential scaling with particle concentration





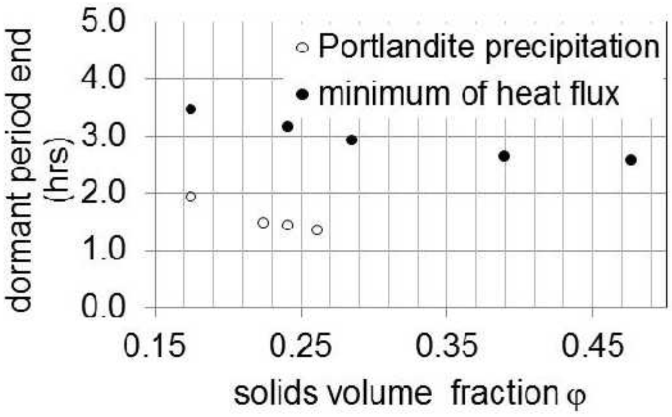
the scaling exponent is a function of microstructure

cement paste undergoes a fast stiffening

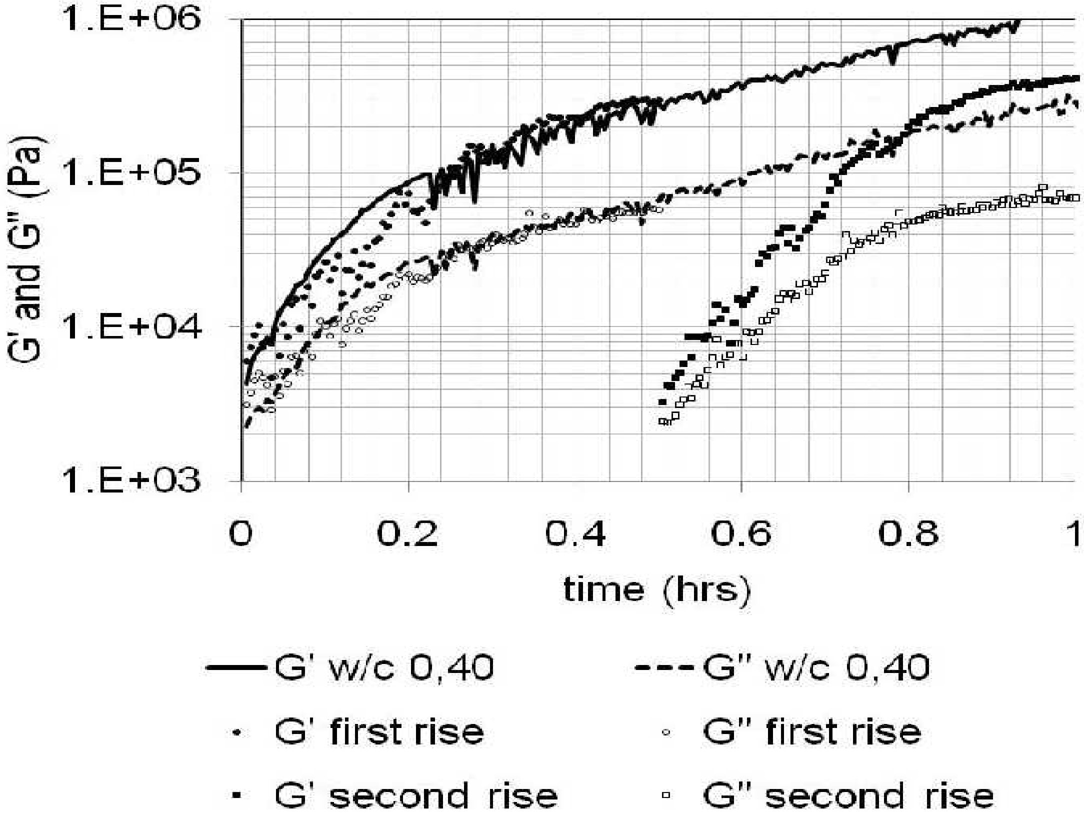


during the dormant period

at Portlandite precipitation there is an upwards inflection



stiffening is reversible before Portlandite precipitation

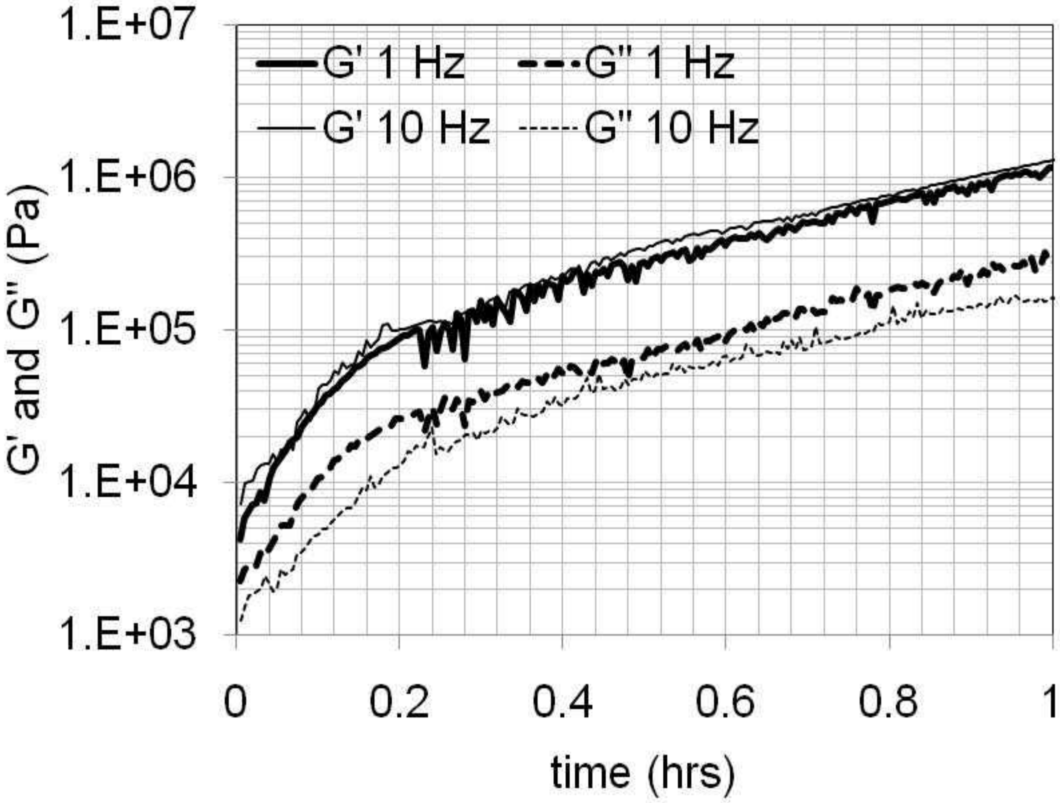


“shearing interrupts aging”

or

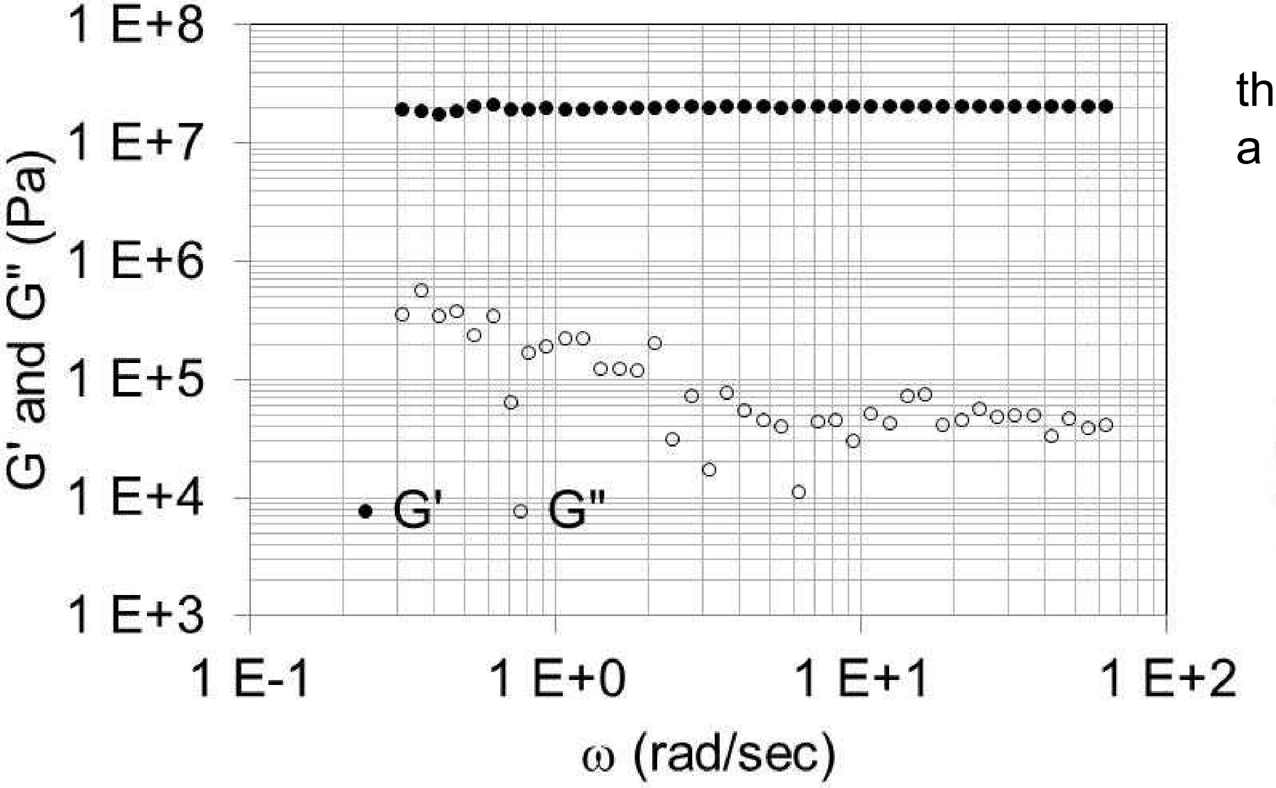
“sharing resets the distribution of heterogeneities”

the loss modulus decreases on increasing frequency

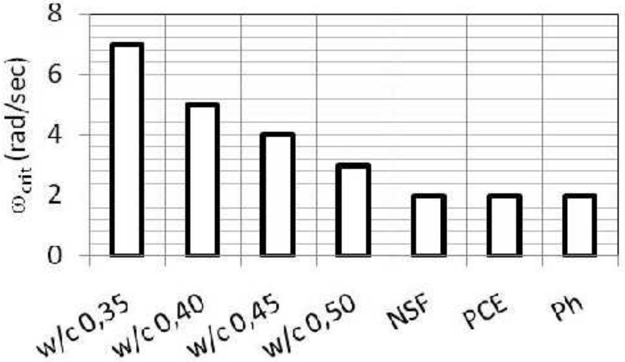


typical of an attractive gel: energy dissipation is due to particle extraction from its local position into the fluid

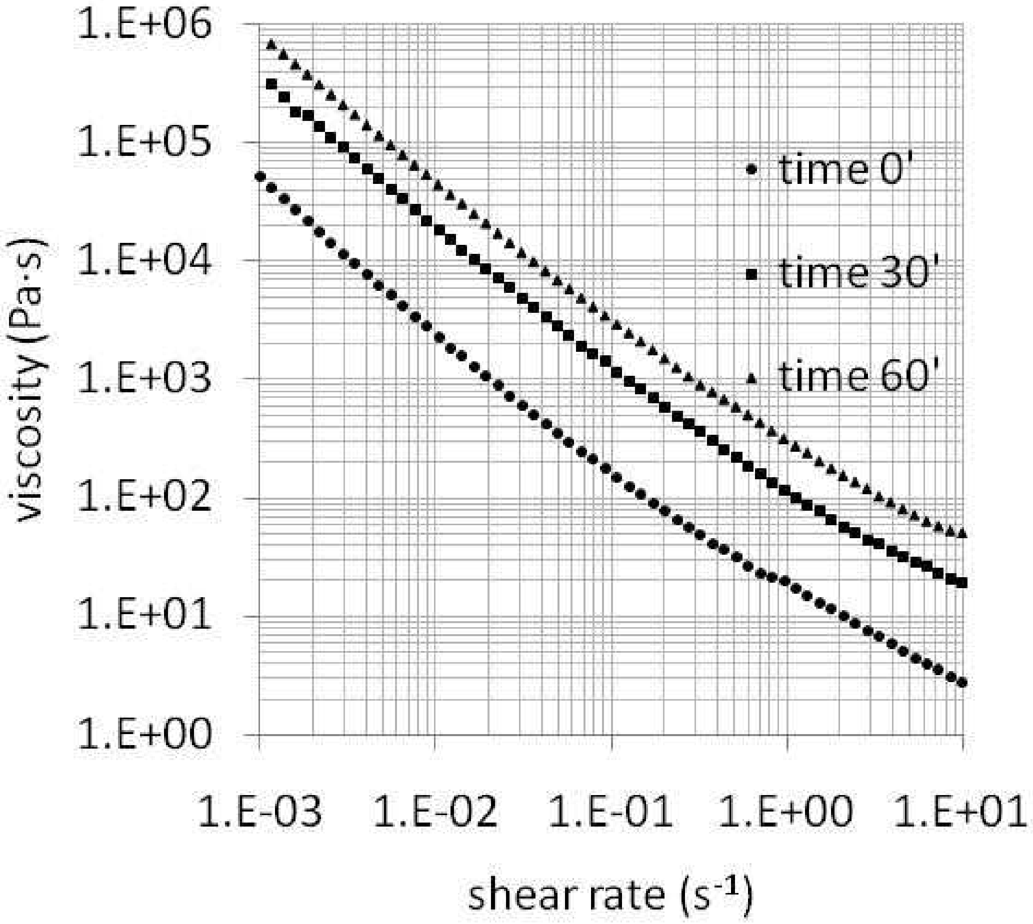
after Portlandite precipitation G’(ω) is constant and G”(ω) decreases up to ωcrit function of concentration



the elastic properties of paste are a function of collective motion



in flow cement paste is shear thinning at low shear rates and shear thickening at high shear rates



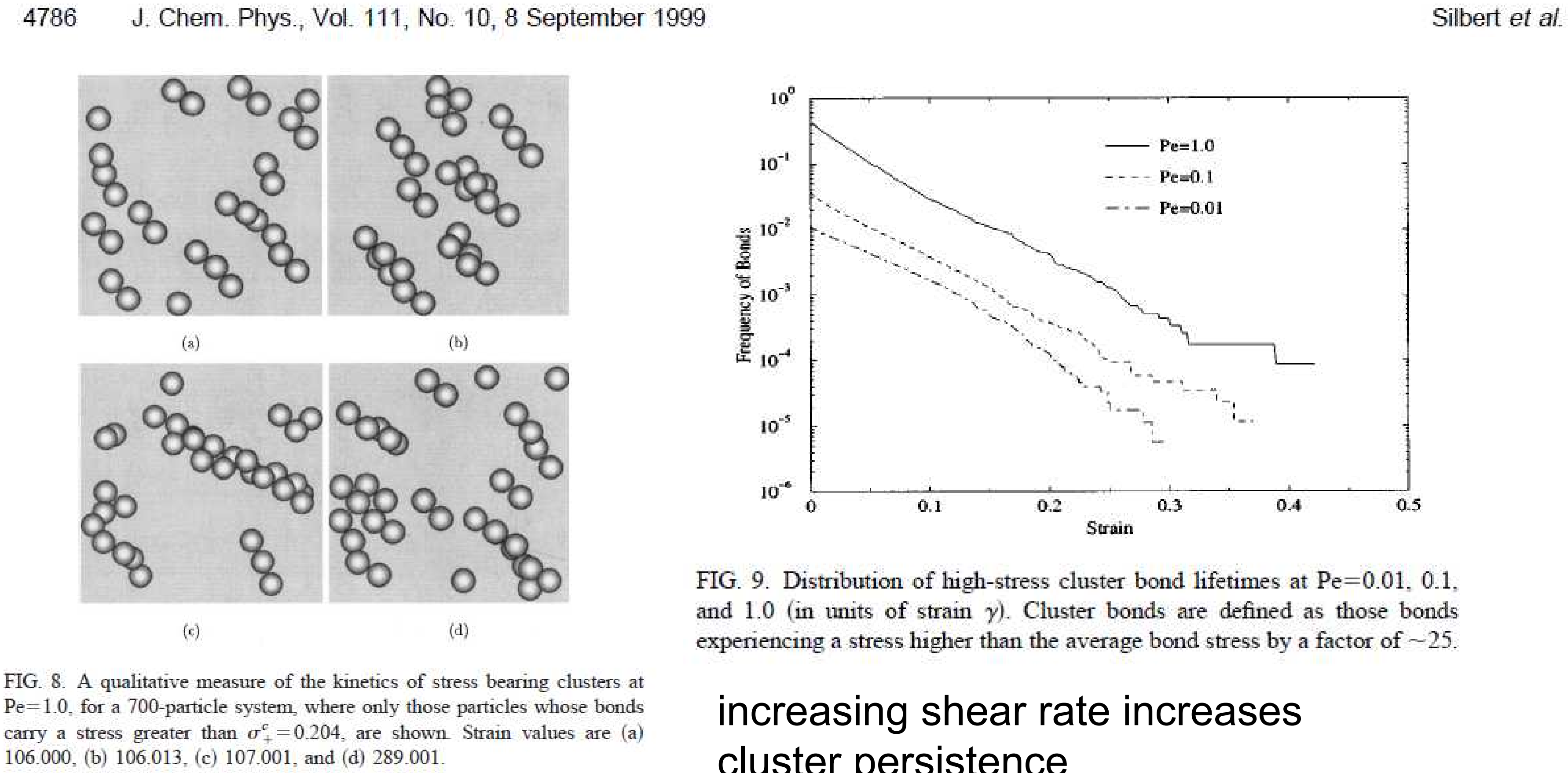
w/c 0,48
$\Phi = 0,40$

viscosity increases over time, as a function of the shear imposed before measuring

shear thinning can be explained by:

- stress distribution and the formation of stress bearing structures

(Silbert, Farr, Melrose, Ball)



4786 J. Chem. Phys., Vol. 111, No. 10, 8 September 1999 Silbert *et al.*

FIG. 8. A qualitative measure of the kinetics of stress bearing clusters at Pe=1.0, for a 700-particle system, where only those particles whose bonds carry a stress greater than $\sigma_{+}^{c}=0.204$, are shown. Strain values are (a) 106.000, (b) 106.013, (c) 107.001, and (d) 289.001.

FIG. 9. Distribution of high-stress cluster bond lifetimes at Pe=0.01, 0.1, and 1.0 (in units of strain γ). Cluster bonds are defined as those bonds experiencing a stress higher than the average bond stress by a factor of ~25.

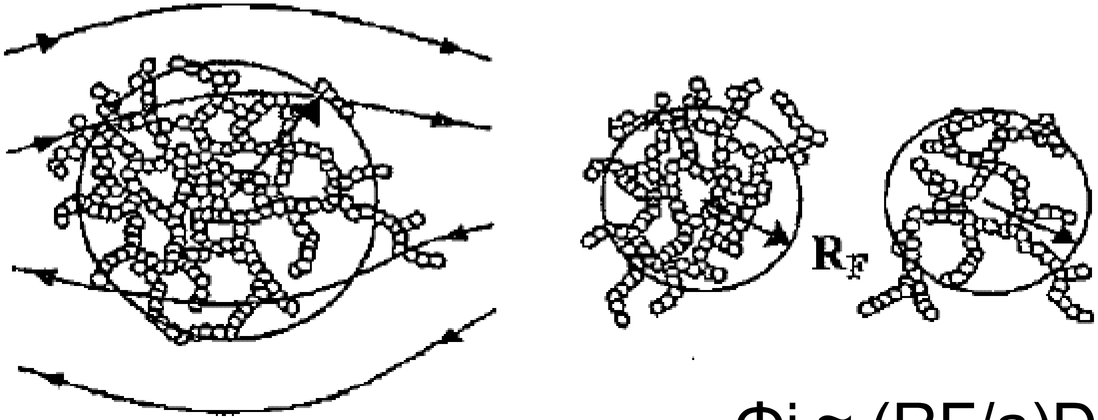
increasing shear rate increases cluster persistence

shear thinning can be explained by:

- agglomerate formation and disruption induced by the hydrodynamic field

(Snabre and Mills; Potanin; Morbidelli et al.)

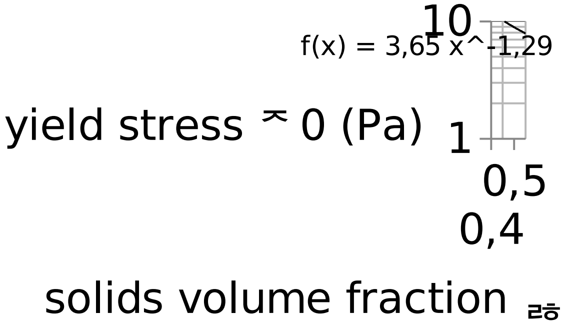
P. Snabre (^{1,*}) and P. Mills (^{2}) JOURNAL DE PHYSIQUE III *September 1996*



$\Phi i \approx (RF/a)D-3$

Fig. 3. — Shear break-up of a fractal cluster into approximately equal parts.

- ⇒ describing the agglomerates does not imply fractal scaling or growth: only density variation with size
- ⇒ fractal dimension is high $D \cong 2{,}8$: aggregates are almost compact, but not homogeneous
- ⇒ this approach delivers the fractal dimension of the agglomerates, related to porosity, and the agglomerate breakup stress, related to interaction energy



- modeling of the agglomerate breakup region gives agglomerate strength, related to interaction energy

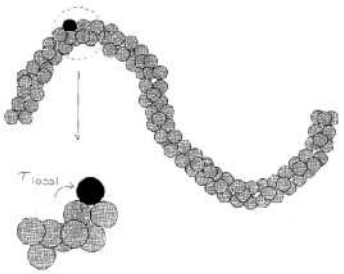
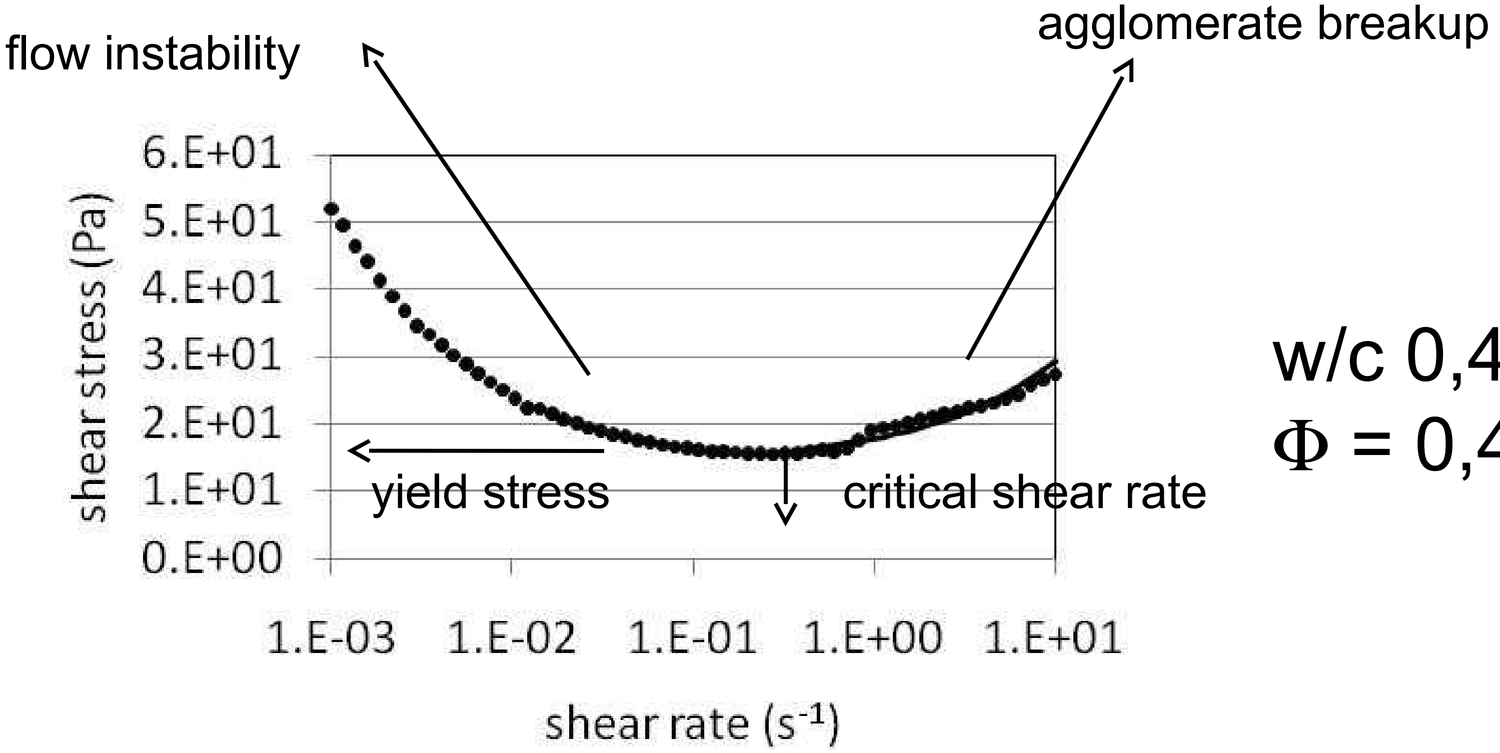


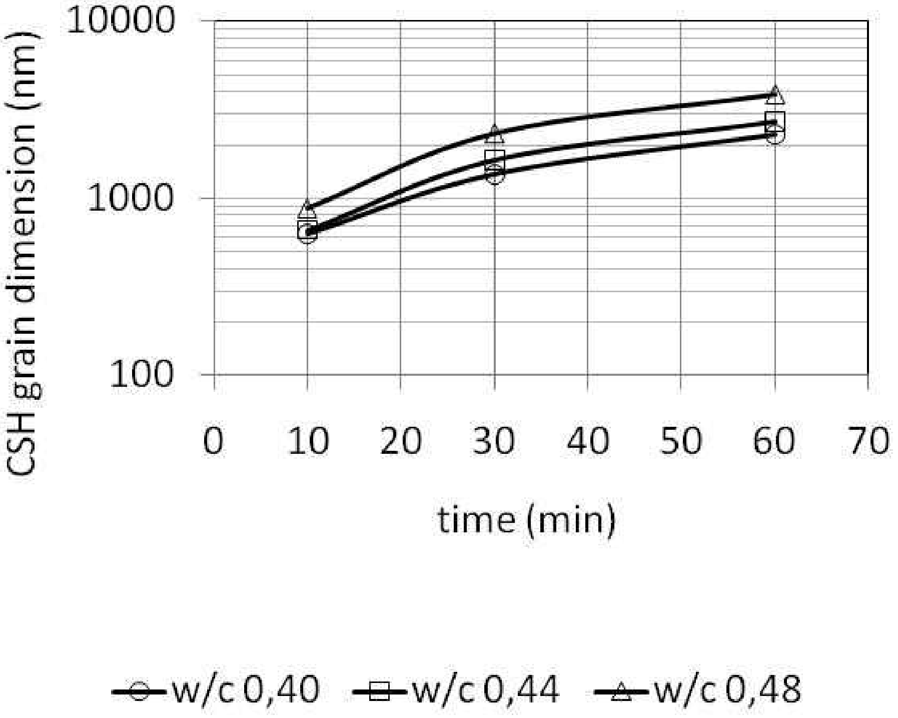
FIG. 1. The multiply connected chain.



w/c 0,48

$\Phi = 0,40$

- in the hypothesis that the connecting surfaces of the elastic chain are C-S-H nuclei it is possible to deduce dimensions



P. Coussot and G. Ovarlez: Physical origin of shear-banding in jammed systems (2010)

The European Physical Journal E

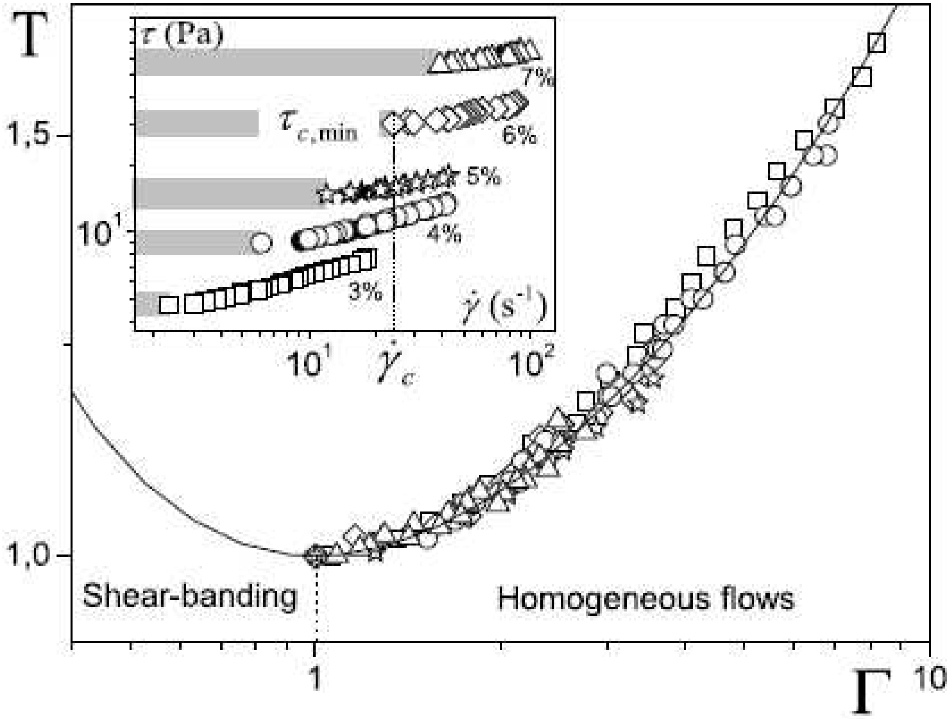
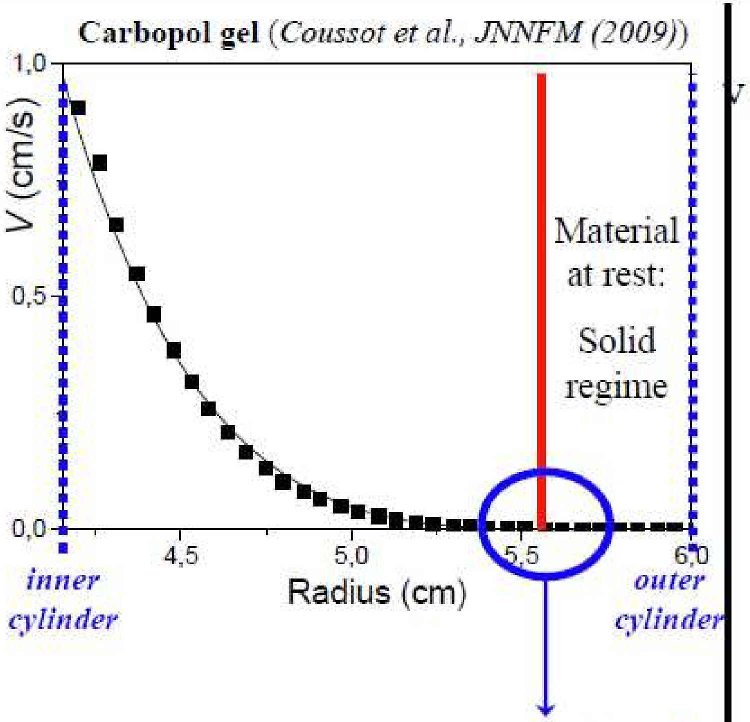


Fig. 5. Flow curves for bentonite suspensions at different solid fractions in terms of dimensionless shear rate and shear stress (see text). The continuous line is the model fitted to data with $n = 0.36$. Inset: effective flow curves (filled and empty symbols correspond to different rotation velocities of the inner cylinder); no steady flow in the grey regions.

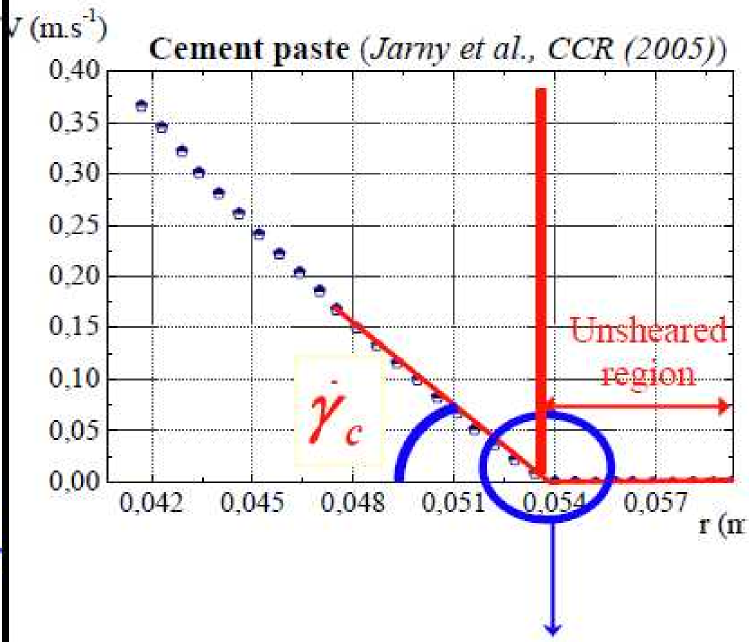
Shear localization / Shear banding in a heterogeneous stress field



Carbopol gel (*Coussot et al., JNNFM (2009)*)

$\tau \rightarrow \tau_Y$ and $\dot{\gamma} \rightarrow 0$

Mostly « **simple** » yield stress fluids

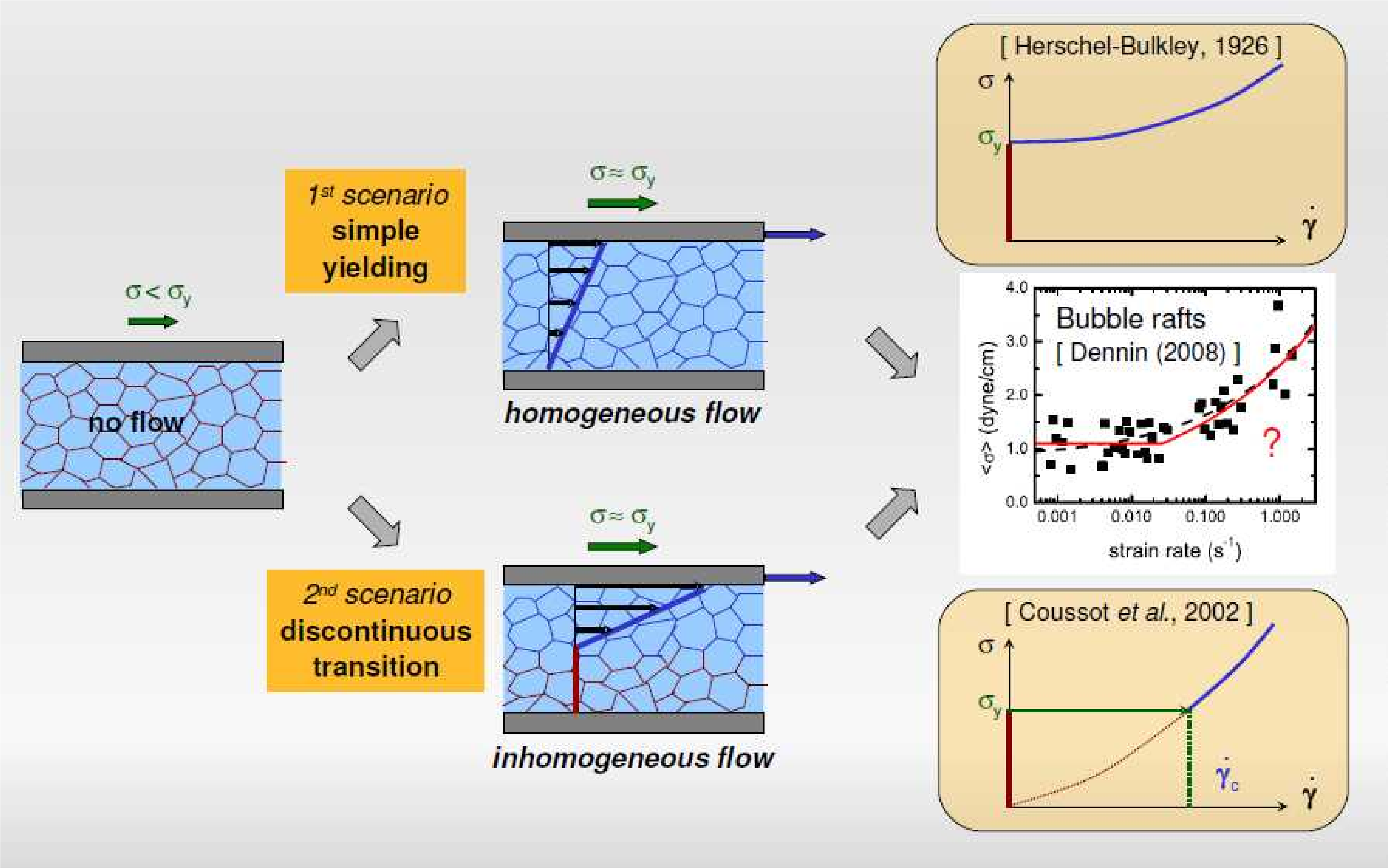


Cement paste (*Jarny et al., CCR (2005)*)

$\tau \rightarrow \tau_Y$ and $\dot{\gamma} \rightarrow \dot{\gamma}_c$

Mostly **thixotropic** yield stress fluids
⇐ competition between **structuration**
and **shear-induced destructuration**

flow instability and shear banding



1st scenario **simple yielding**

2nd scenario **discontinuous transition**

homogeneous flow

inhomogeneous flow

admixtures to improve cohesivity and robustness of SCC

Component	kg/m^3
cement CEM II/A-M (LL-S) 42,5 R	429
limestone filler	90
sand 0/2 mm	860
aggregate 4/8 mm	264
aggregate 8/16 mm	605
water	189

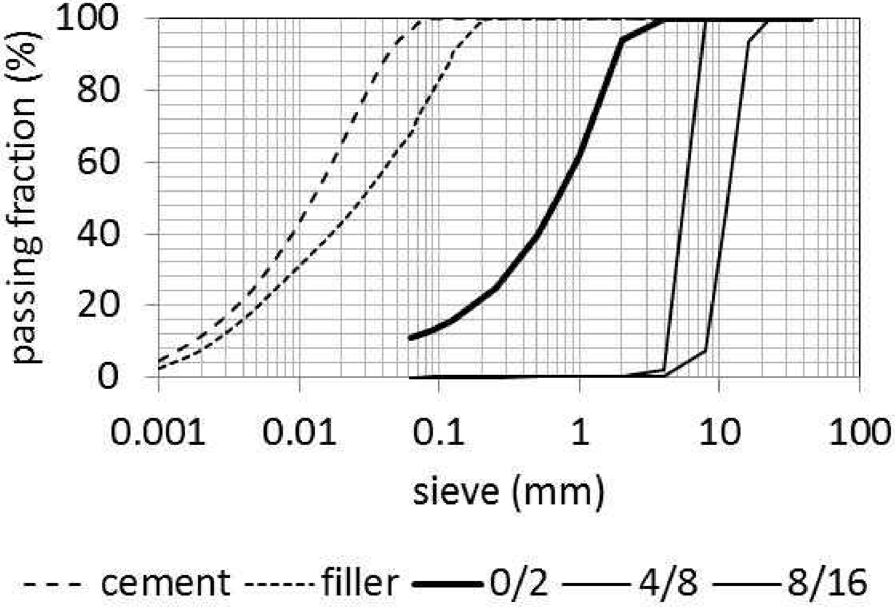
paste: 362 l/m3

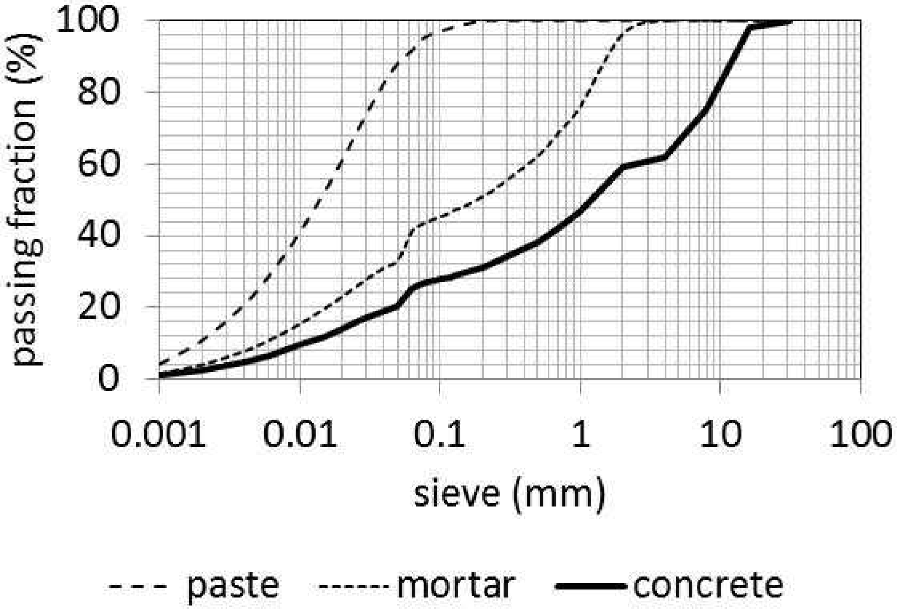
water/fines by weight: 0,36 water/fines by volume: 1,09

paste solids volume fraction: 0,48

sand/all aggregates: 0,5

admixtures to improve cohesivity and robustness of SCC





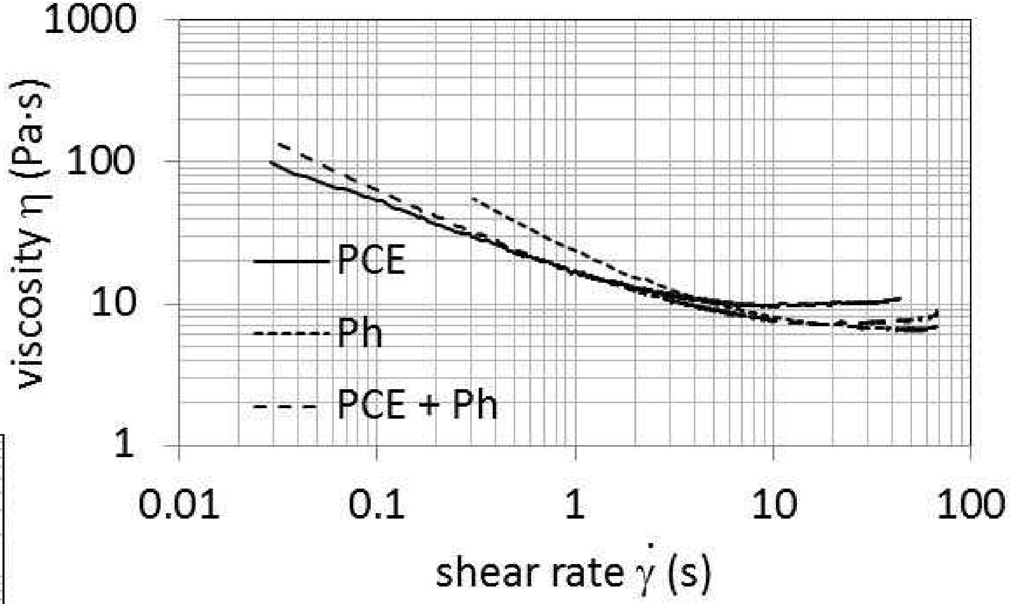
admixtures to improve cohesivity and robustness of SCC

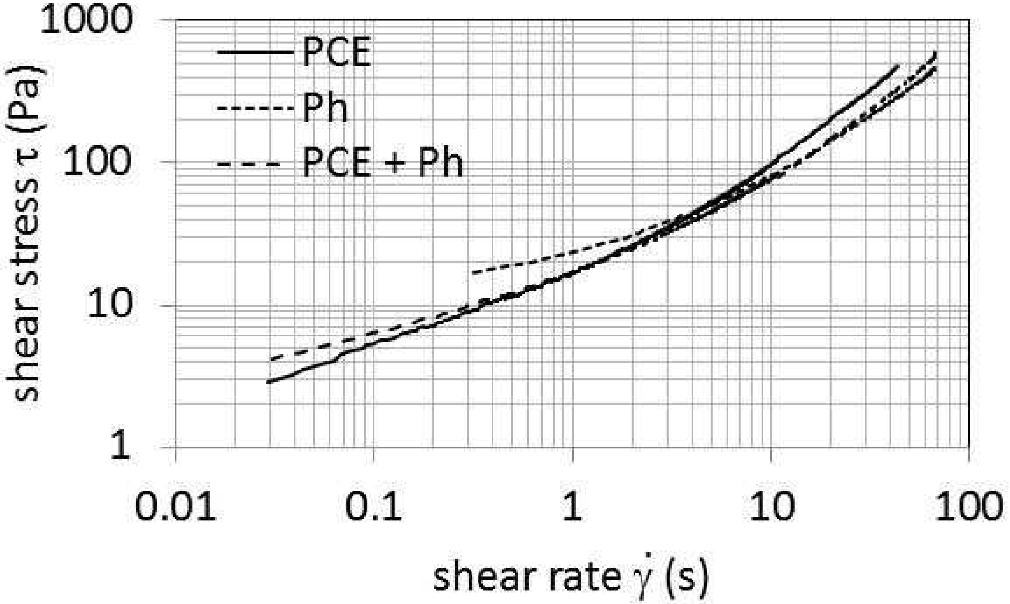
property	PCE	Ph	PCE + Ph
slump flow (mm)	700	700	715
T_{500} (s)	3,3	2,9	2,6
V-funnel flow time (s)	8,5	6,3	6,5
L-box passing ratio	0,73	0,75	0,80

admixture dosage:	PCE	3,66 kg/m3 of a 24% solution
	Ph	6,41 kg/m3 of a 30% solution
	PCE+Ph	5,04 kg/m3 of a 28% solution

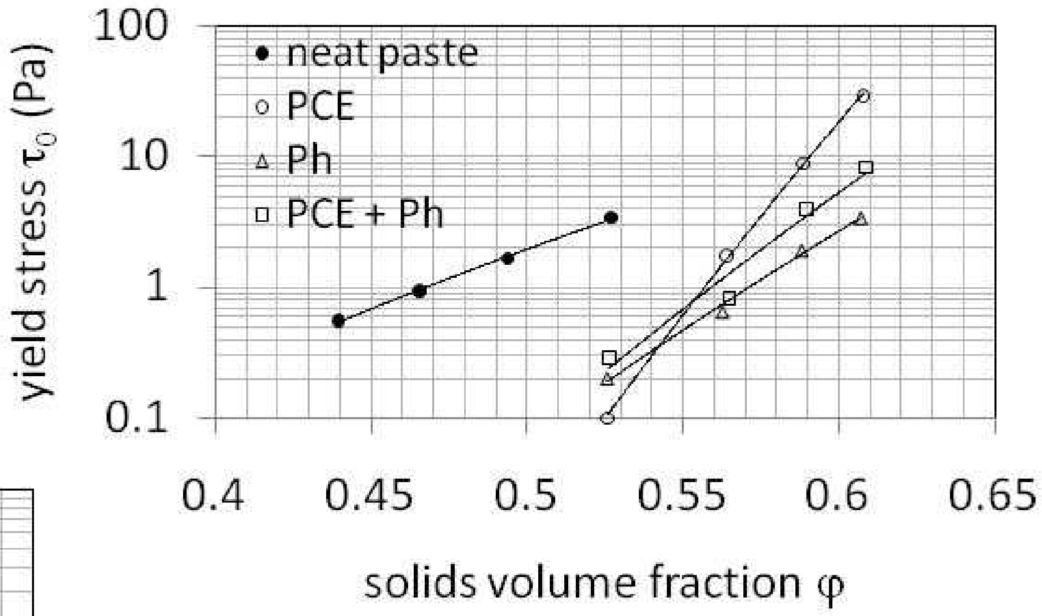
blend PCE + Ph: 36% PCE + 64% Ph as dry matter

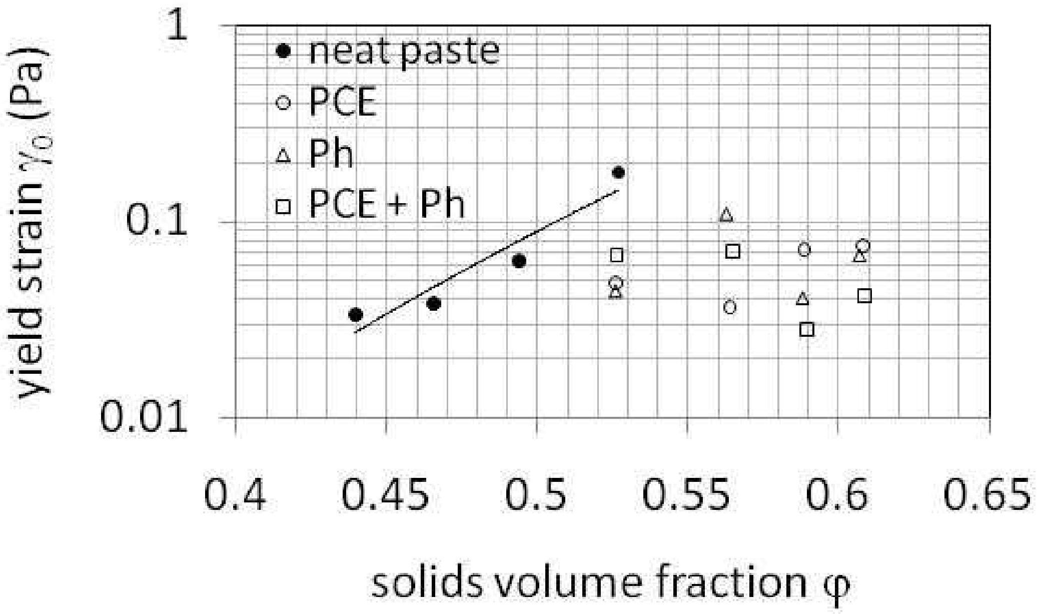
rheology of the mortar





rheology of the paste

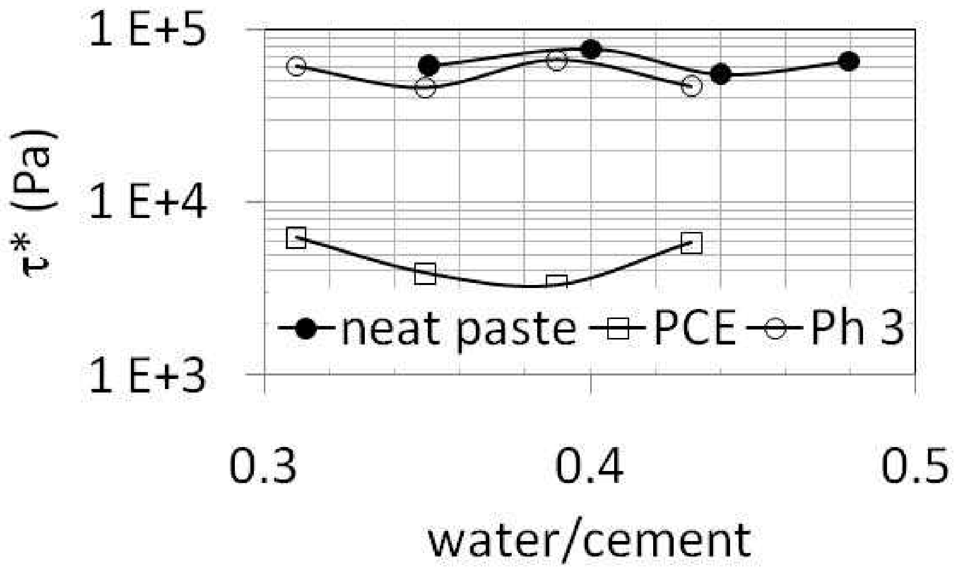




rheology of the paste

paste	neat	PCE	Ph	PCE + Ph
yield stress scaling exponent	9,98	39,1	20,0	23,6
yield strain scaling exponent	9,21	≈ 0	≈ 0	≈ 0

suggesting a different paste microstructure and inter-particle strength



concluding remarks

- cement paste rheology is controlled entirely by the attractive particle interactions in the dormant period
- the presence of superplasticizers modifies rheology but also microstructure – heterogeneity distribution

thank you!