Homogenization as a microstructure probe tool a journey to the interior of cement paste

From concrete nanoscale to structure celebrating Gilles CHANVILLARD's memory

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Introduction

Cementitious materials

- have time-dependent properties
- are multi-scale
- host multi-physics processes
- interact with their environment

Homogenization

- can bridge scales: physical processes $\rightarrow$ engineering behaviour
- can estimate microstructure influence on macroscopic properties

But cement paste microstructure

- is difficult to comprehensively observe in its multiscale nature
- may be too complex to be accurately modelled in full details

And cement paste macroscopic properties

- are easy to measure
- are of direct interest for engineers

General strategy

- “focus on first order effects”
  start with a simplified morphological model
- “equations have to be nice and efficient”
  use mean-field homogenization
- “be demanding on model validation”
  compare predictions to experimental measurements
- iterate this trial-and-error process
  - comparison OK ⇒ get other experimental data to compare
  - comparison KO ⇒ go back to morphological model and improve it

Outline

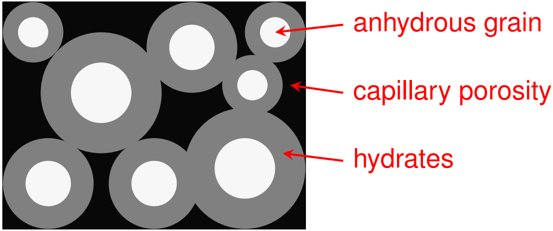
Outline

Hydrates growing around cement grains

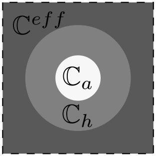
Simplified view of cement paste

3 phases: anhydrous, hydrates, capillary porosity

A common morphological model

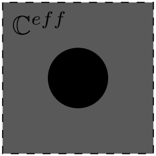


Generalized self-consistent scheme



heterogeneous solid phase (morphologically representative pattern: layered sphere)

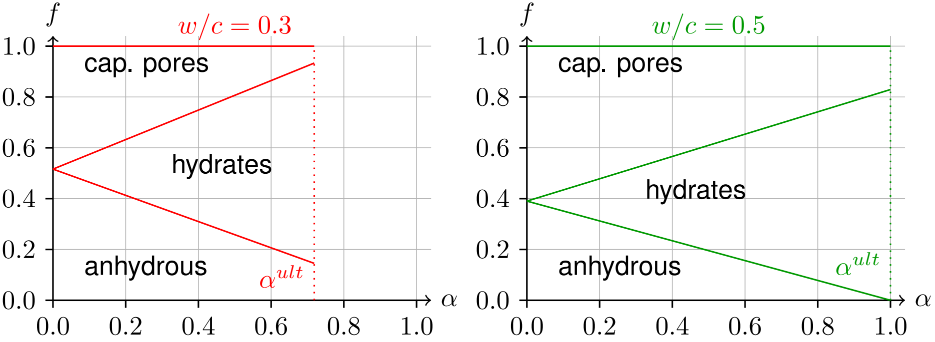
+



capillary porosity (sphere)

Input data: phases volume fractions and elasticity

Hydration: Powers model [Powers et al., JACI 43, 1946]

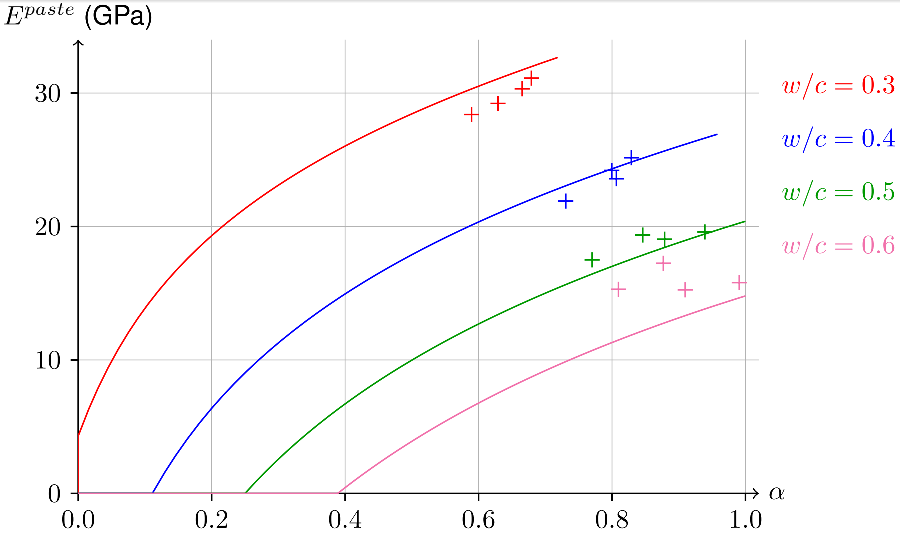


Elastic properties

	E (GPa)	ν	source
anh.	135	0.3	nano-indentation[1]
hyd.	31	0.24	nano-indentation[2]

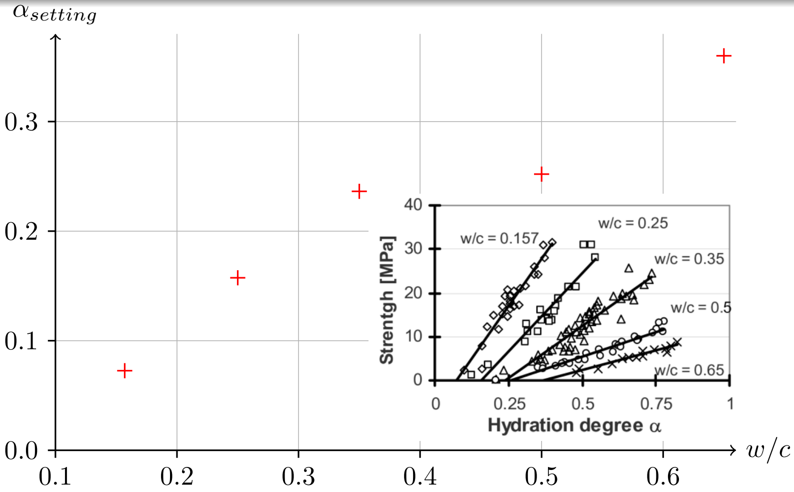
[1] [Velez et al., CCR 31, 2001], [2] [Velez et al., Kurdowski symp., 2001]

Effective stiffness from MRP-based model



Experimental data on cement pastes [Haecker et al., CCR 35, 2005]

Experimental estimation of setting degree of hydration

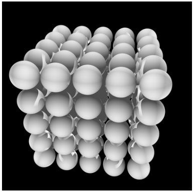


Experimental data: linear regression [Torrenti et al., MaS 38, 2005], strength data [Byfors, PhD, 1980] and [Taplin, AJAS 10, 1959]

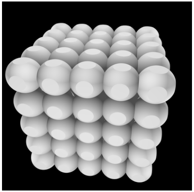
An attempt to interpret SCS implicit morphology

Interpenetrating spheres on primitive cubic lattice

FEM computations $\Rightarrow k^{eff}$



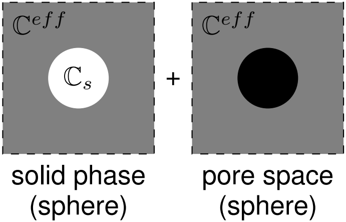
$\varphi = 0.6$



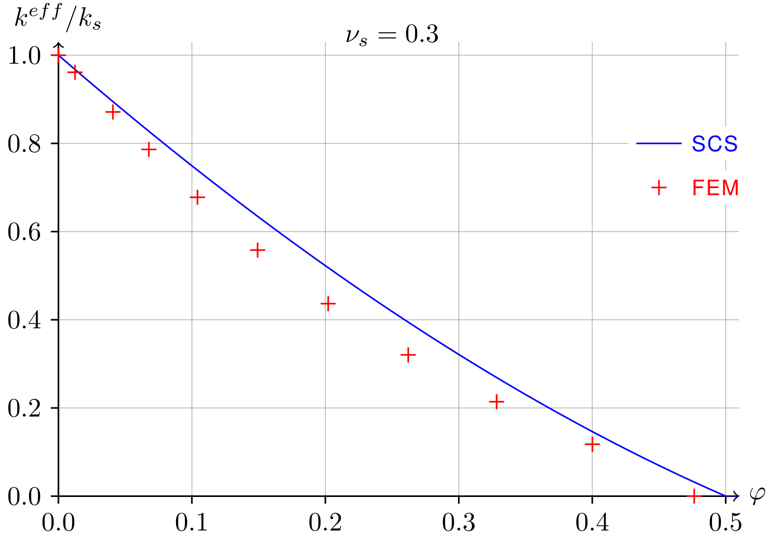
$\varphi = 0.3$

Self-consistent scheme

$\Rightarrow \mathbb{C}^{eff}$



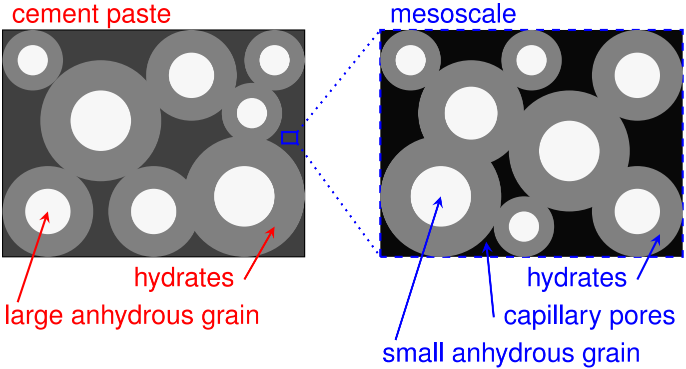
Self-consistent scheme vs spheres on cubic lattice



Towards a multiscale description

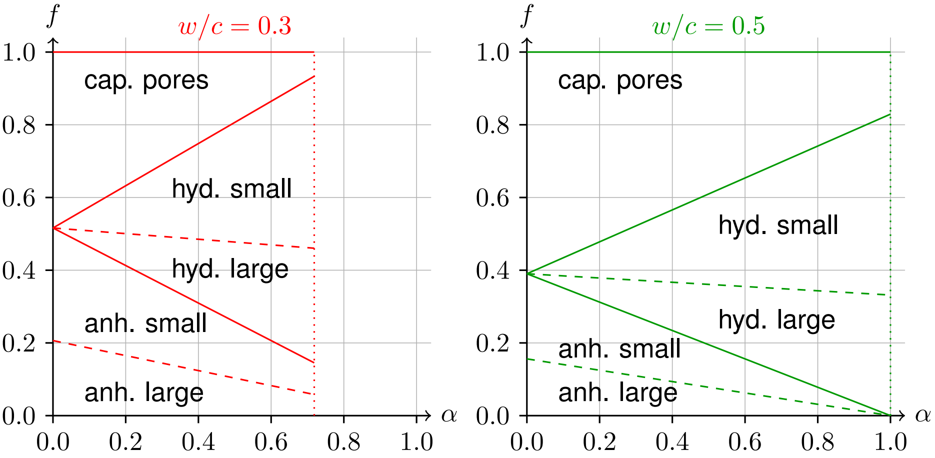
Current morphological model ≈ monodisperse distribution of spheres
⇒ instantaneous setting for $w/c < 0.32$

To mitigate this issue: multiscale description of cement grains starting with two separated scales

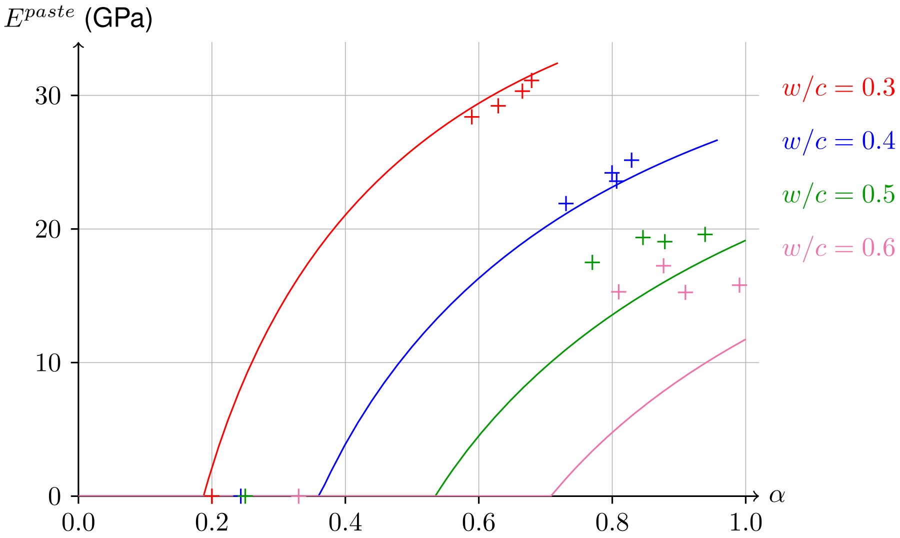


Phases volume fractions

Hydration: Powers + hydration rate size-independent (simplification)
small particles: $60\ \%$



Effective stiffness from 2-scales MRP-based model



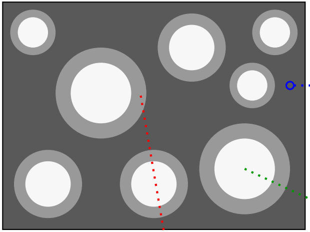
Outline

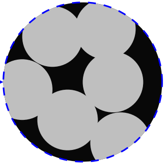
Setting controlled by outer hydrates

Completely avoid instantaneous setting

consider cement grains as inclusions in a matrix

Introduction of high/low density hydrates as inner/outer products

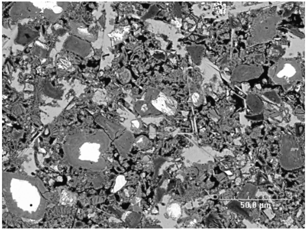




low density hydrates (outer)

precipitation of hydrate solids (spheres)

anhydrous

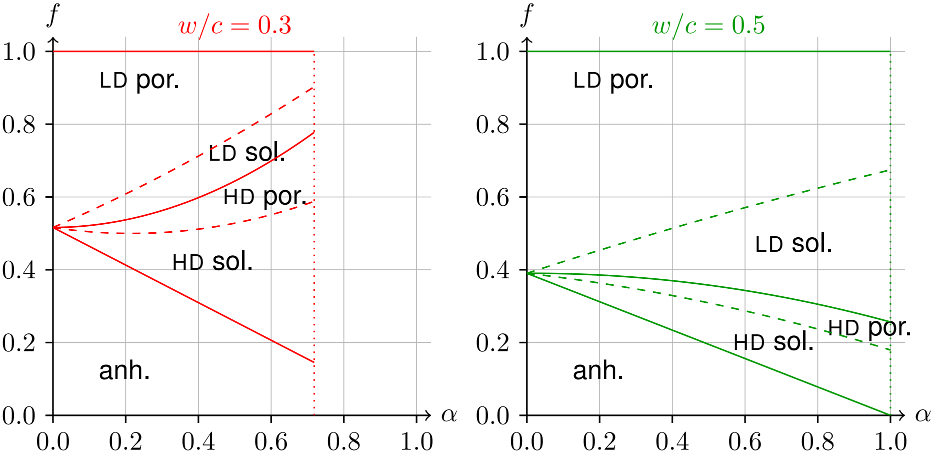


high density hydrates (inner)

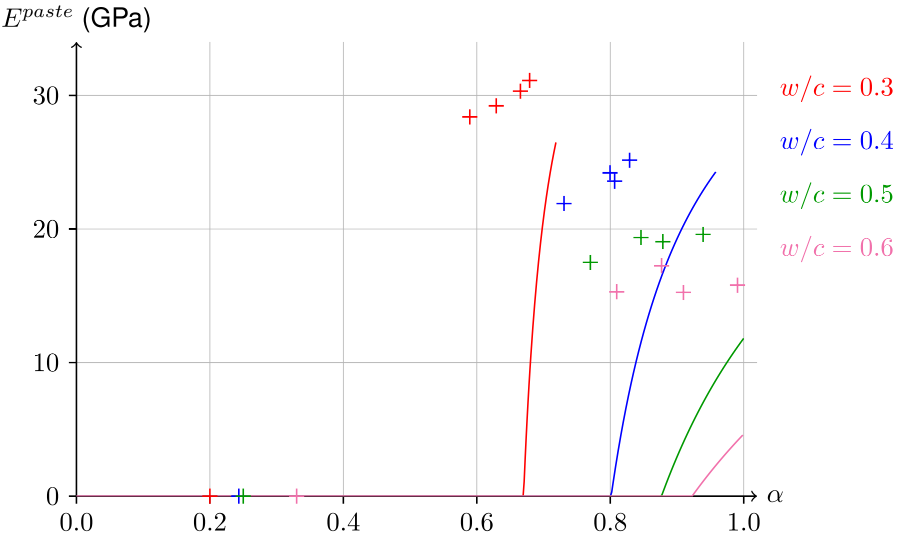
Setting of outer $\Rightarrow$ setting of paste

Hydration with HD and LD hydrates

Hydration: Powers model
+ repartition HD / LD hydrates [Tennis et al., CCR 30, 2000]
+ $\varphi_{hd} = 0.3$ (from 0.28 [Powers] to $0.30, 0.35$ [Tennis et al., CCR 30, 2000])



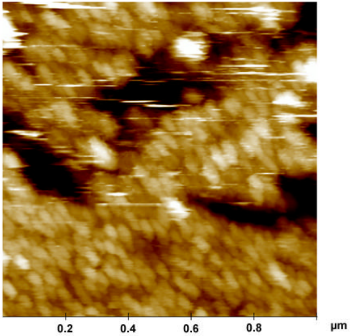
Effective stiffness from inner/outer model



Is the spherical shape relevant for hydrate solids?

AFM observation of a C_3S crystal covered by a lime-saturated droplet

[Garrault-Gauffinet, PhD, 1998]



Small particules of C-S-H
anisotropic shape

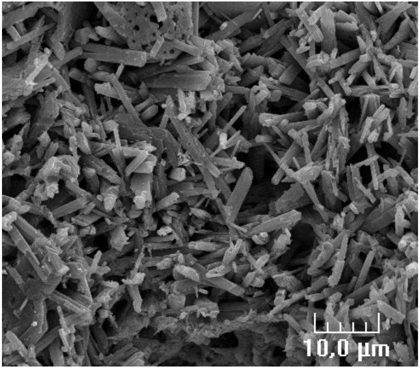
- parallel to the grain surface
  60 nm by 30 nm
- thickness: 5 nm

$\Rightarrow$ elementary bricks of C-S-H
aspect ratio $r_s = 5/\sqrt{30 * 60} \approx 0.12$

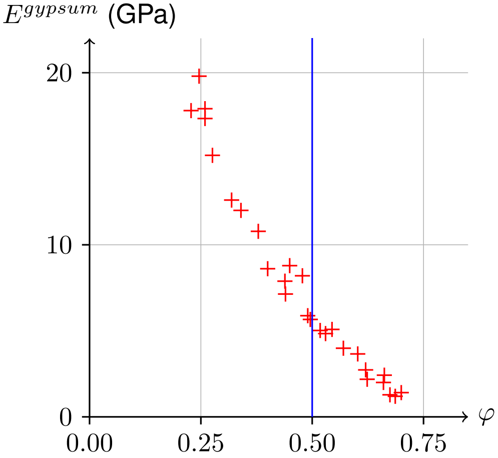
Question of the morphology of C-S-H still widely opened

we chose a representation based upon these elementary bricks

The gypsum “interlude”



Gypsum: elongated crystals

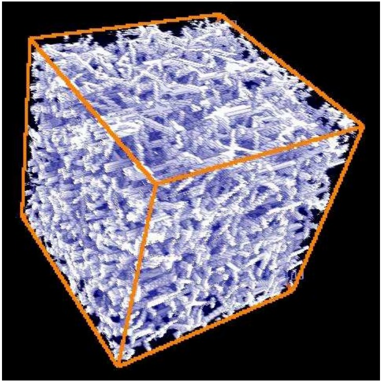


Experimental data on gypsum [Meille, PhD, 2001], [Colak, ML 60, 2006], [Ali et al., JMS 10, 1975], [Phani, ACSb 65, 1986], [Tazawa, ACBM 7, 1998]

An attempt to take into account elongated particles

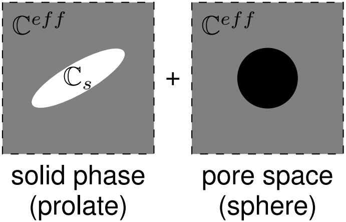
elongated particles, random orientation

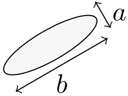
Parallelepipeds (21*3*3 voxels)
randomly put into a cube
FEM computations



[Meille, PhD, 2001]

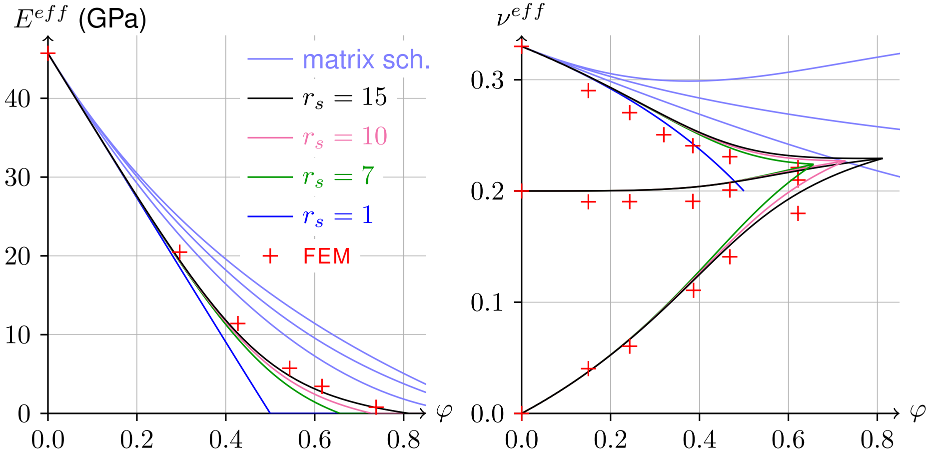
Self-consistent scheme
solid inhomogeneity = prolate spheroid
+ isotropic orientation distribution





aspect ratio
$r_s = b/a > 1$

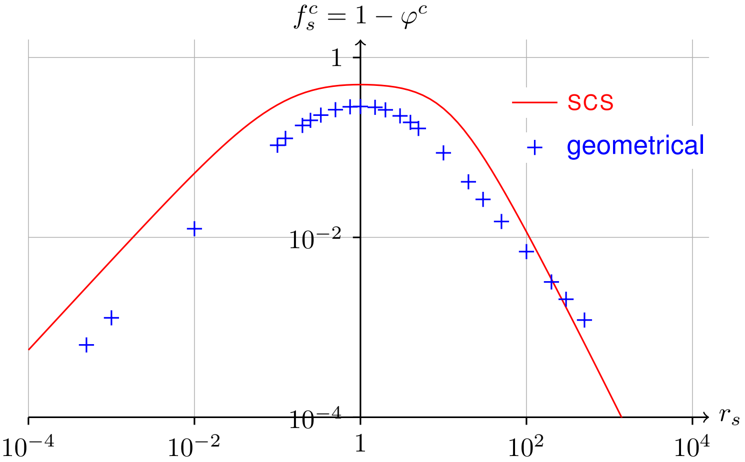
SCS with prolate-shaped solid VS FEM



Critical porosity $\varphi^c = 1 - f_s^c$ depends on prolate aspect-ratio r_s

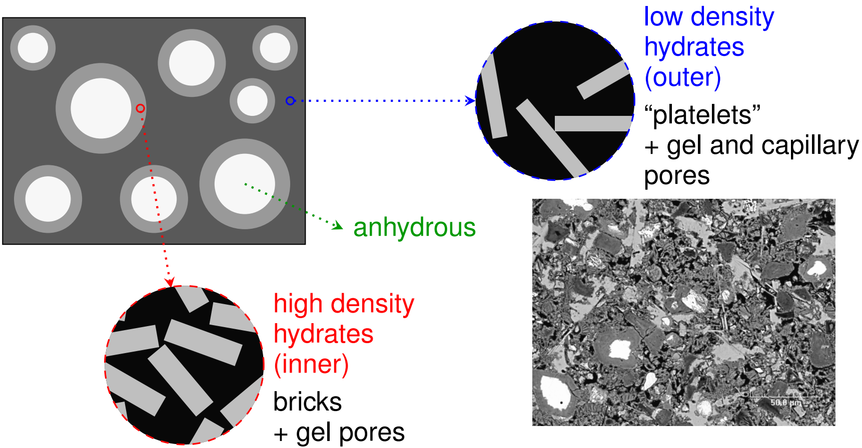
FEM results [Meille, PhD, 2001]

SCS critical solid volume fraction VS geometry



Geometrical percolation of spheroids [Garboczi et al., PRE 52, 1995]

Oblate-shaped hydrate solids



Input data: elastic and morphological parameters

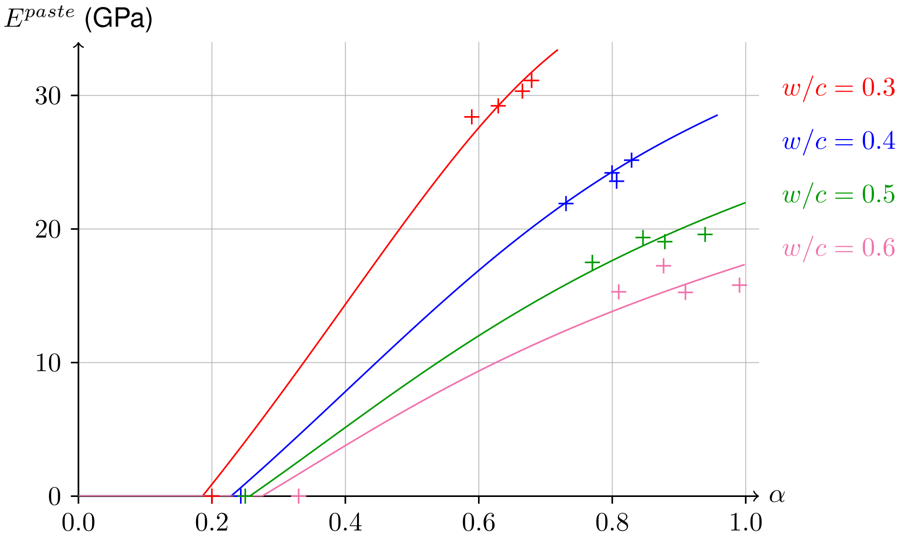
	E (GPa)	ν	φ	a.r.	source
anh.	135	0.3			nano-indentation[1]
hyd. HD	31	0.24	0.3	0.12	nano-indentation[2], porosity[3], AFM[4]
hyd. LD	evol.	evol.	evol.	0.033	self-consistent scheme, hydration model, setting
hyd. solids	71.6	0.27			reverse analysis hyd. HD

LD aspect-ratio: fit on setting results

Rem: atomic scale modelling [Pellenq et al., CCR 38, 2008]
tobermorite C/S=0.83
Young's modulus: 54 (⊥ sheets); 68, 72 (∥ sheets) GPa

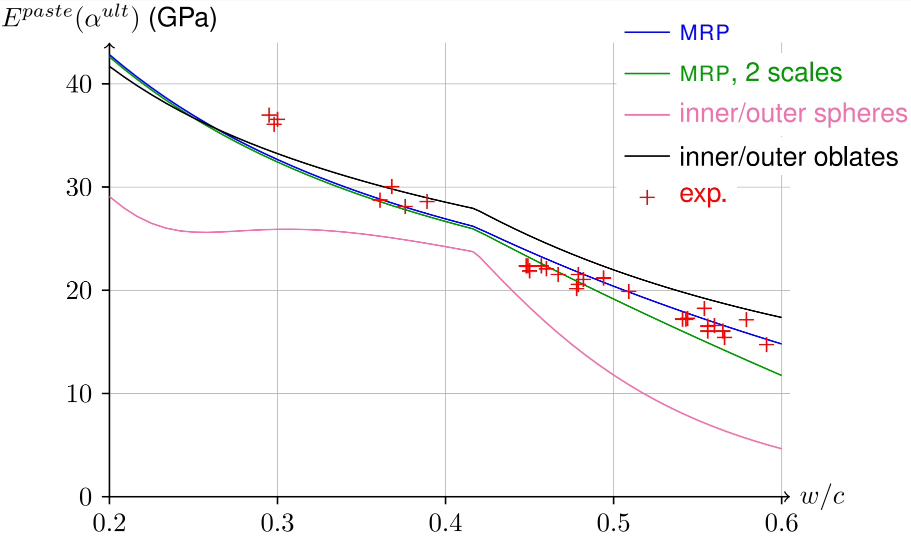
[1] [Velez et al., CCR 31, 2001], [2] [Velez et al., Kurdowski symp., 2001], [3] [Tennis et al., CCR 30, 2000],
[4] [Garrault-Gauffinet, PhD, 1998]

Effective stiffness from inner/outer with bricks/platelets



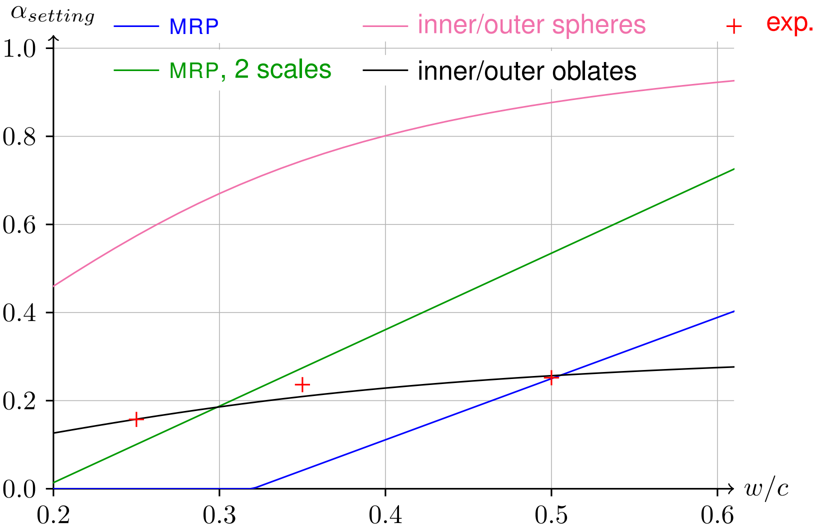
Outline

Mature pastes: $\alpha = \alpha^{ult}$



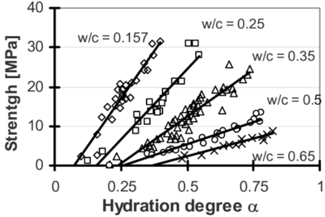
Experimental data [Helmuth et al., Symp. Struct. of Portl. C.P. and Concr., 1966]

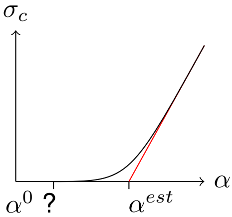
Hydration degree at setting

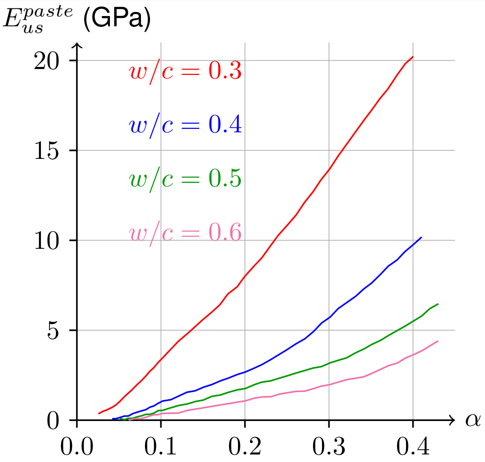


Experimental data [Torrenti et al., MaS 38, 2005]

Setting: more insights at early age



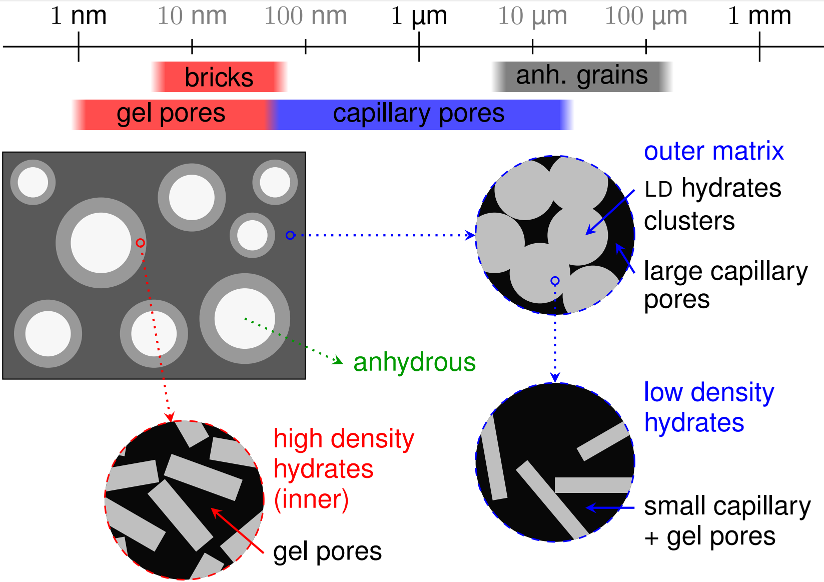




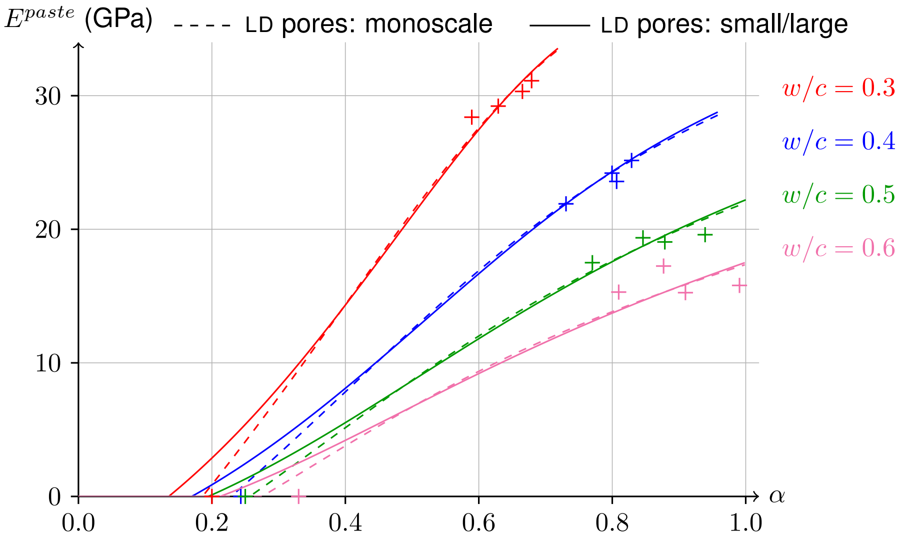
Continuous monitoring of stiffness, from fluid state?

- Ultra-sonic meas. [Boumiz et al., 2nd Rilem workshop on hydration and setting, 1997]
- EMM-ARM technique [Azenha et al., CCR 40, 2010]

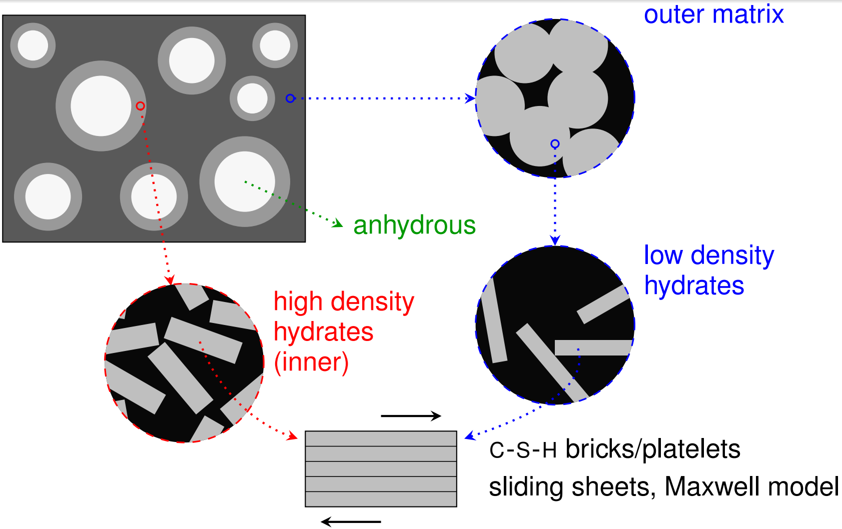
Scale separation in outer hydrates



Effective stiffness from 2-scales outer



Converting elastic model to basic creep model

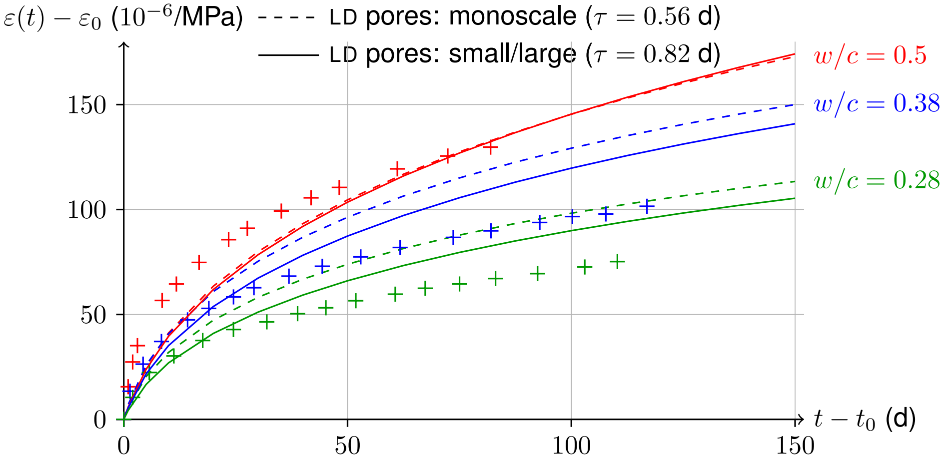


Only one extra parameter: Maxwell sliding characteristic time τ

Creep of cement paste VS experimental data

Assumption: frozen microstructure ($\alpha = \alpha^{ult}$)

$\Rightarrow$ Laplace-Carson transform: non ageing viscoelasticity $\rightarrow$ elasticity



Experimental data on cement pastes (28 d) [Le Roy, PhD, 1995]

Thanks Gilles

A morphological model of cement paste

- simplified (hydrates not detailed)
- efficient (mean field homogenization)
- validated (at both early and late ages)
- not just about elasticity prediction (can be extended to creep)

Many sources of improvement and prospects

- morphology: differentiate mineral phases + upscale to concrete
- improve chemical modelling
  (hydration, degradation mechanisms, . . .)
- more experimental comparisons
- investigate other mechanical properties
  (creep, strength, damage, . . .)
- investigate transport properties

Paper co-authored with Gilles on cement paste

For more details

- J. SANAHUJA, L. DORMIEUX and G. CHANVILLARD. Modelling elasticity of a hydrating cement paste. *Cement and Concrete Research*, 37(10):1427–1439, 2007.