**Nanostructure and Nanomechanics of Cement: Polydisperse Colloidal Packing**

The MIT Faculty has made this article openly available. Please share how this access benefits you. Your story matters.

<table>
<thead>
<tr>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>As Published</td>
<td><a href="http://dx.doi.org/10.1103/PhysRevLett.109.155503">http://dx.doi.org/10.1103/PhysRevLett.109.155503</a></td>
</tr>
<tr>
<td>Publisher</td>
<td>American Physical Society</td>
</tr>
<tr>
<td>Version</td>
<td>Final published version</td>
</tr>
<tr>
<td>Citable Link</td>
<td><a href="http://hdl.handle.net/1721.1/76305">http://hdl.handle.net/1721.1/76305</a></td>
</tr>
<tr>
<td>Terms of Use</td>
<td>Article is made available in accordance with the publisher’s policy and may be subject to US copyright law. Please refer to the publisher’s site for terms of use.</td>
</tr>
</tbody>
</table>

Detailed Terms

MIT OPEN ACCESS ARTICLES

DSpace@MIT

MASSACHUSETTS INSTITUTE OF TECHNOLOGY
Nanostructure and Nanomechanics of Cement: Polydisperse Colloidal Packing

E. Masoero,1 E. Delgado,2 R. J.-M. Pellenq,1,3 F.-J. Ulm,1 and S. Yip4
1Department of Civil and Environmental Engineering, Massachusetts Institute of Technology, Cambridge, Massachusetts 02139, USA
2Department of Civil, Environmental and Geomatic Engineering, ETH Zürich, 8093 Zurich, Switzerland
3CINaM, CNRS and Aix-Marseille University, Campus de Luminy, 13288 Marseille Cedex 09, France
4Department of Nuclear Science and Engineering, Massachusetts Institute of Technology, Cambridge, Massachusetts 02139, USA

(Received 6 December 2011; revised manuscript received 23 March 2012; published 10 October 2012)

Cement setting and cohesion are governed by the precipitation and growth of calcium-silicate-hydrate, through a complex evolution of microstructure. A colloidal model to describe nucleation, packing, and rigidity of calcium-silicate-hydrate aggregates is proposed. Polydispersivity and particle size dependent cohesion strength combine to produce a spectrum of packing fractions and of corresponding elastic properties that can be tested against nanoindentation experiments. Implications regarding plastic deformations and reconciling current structural characterizations are discussed.

DOI: 10.1103/PhysRevLett.109.155503 PACS numbers: 62.25.-g, 62.20.De, 82.70.Dd

The cohesive strength of concrete arises from the hardening of cement paste, produced by mixing cement powder with water (hydration) and allowing time for setting. Hydration and setting encompass dissolution and precipitation at the molecular scale, growth of hydration products up to the micron scale, and rigidity percolation through micron to millimeter size cement powder grains [1,2]. The mechanics of cement setting is believed to be governed by the properties of the hydration product calcium-silicate-hydrate (C-S-H), which forms a nanoporous highly cohesive phase, that glues together the different components. While controlling the development of the C-S-H structure and its subsequent evolution is the key to advance cement technology, it is still fundamentally not known how the mesoscale organization develops, from the nanometer scale to the stress-bearing submicron structure, and how this determines the mechanical behavior of the cement paste [1].

The nature of C-S-H itself is elusive and complex. Recent studies suggest that during the precipitation of hydration products, C-S-H clusters aggregate on the nanoscale, due to net attractive electrostatic forces, giving rise to a colloidal type of gel already at relatively low densities [3,4]. This evolves, during setting, into a dense mature microstructure, whose nanoscale mechanics is suggestive of a jammed packed assembly of rigid grains [5], which also indicates a highly heterogeneous structure in terms of local density. Within this scenario, there is a need to elucidate the interplay between cohesive interactions and packing, in analogy to colloidal gels and glasses [6,7].

We study C-S-H precipitation and aggregation using a primitive model of space filling of cohesive nanoscale, colloidal units. Previous works [3,4,8] support such simplification, in order to capture the underlying physical mechanisms. We show that this approach can span length scales from nanometer sized C-S-H aggregates up to mesoscale sub-micron organization. Using Monte Carlo simulations, we calculate the elastic moduli measured in nanoindentation tests and obtain results in the same range as existing experiments. We demonstrate the experimentally observed wide range of C-S-H local densities can be associated with the polydispersity of the C-S-H aggregates, formed during dissolution and precipitation. Furthermore, our study clarifies the role of the polydispersity of C-S-H clusters, as well their strong cohesive interactions. Our results support the idea that C-S-H is akin to a very heterogeneous medium, an amorphous strongly cohesive solid with dynamical features typical of slowly evolving, aging glassy materials. Within this picture, local irreversible structural rearrangements could manifest in a granular-type of mechanical response, as the one observed in nanoindentation tests [5,9].

We model an open system of C-S-H particles with a uniform size distribution, from a minimum \( \sigma_m \) to a maximum \( \sigma_M \) value. Among other possible definitions (see, e.g., Ref. [10]), we choose the standard deviation \( \sigma \) of the initial distribution in units of \( 1/2(\sigma_M + \sigma_m) \) as the measure of polydispersity. The nature of effective interactions in C-S-H is still a subject of intensive investigation, as experiments and atomistic simulations suggest a narrow attractive potential would be appropriate [11]. We adopt a generalized Lennard-Jones form for particle interactions:

\[
U_{ij}(r_{ij}) = 4\epsilon(\tilde{\sigma}_{ij}) \left( \frac{\tilde{\sigma}_{ij}}{r_{ij}} \right)^{2\gamma} \left( 1 - \frac{\tilde{\sigma}_{ij}}{r_{ij}} \right)^{\gamma},
\]

where \( r_{ij} \) is the interparticle distance, \( \epsilon(\tilde{\sigma}_{ij}) \) is the well depth between two particles with different size \( \sigma_i \) and \( \sigma_j \), and \( \tilde{\sigma}_{ij} = (\sigma_i + \sigma_j)/2 \). The potential minimum is at \( r_{ij} = r_m = \sqrt{2} \tilde{\sigma}_{ij} \), while the maximum attractive force \( dU_{ij}/dr_{ij} \) occurs at \( r_{ij} = r_a = \sqrt{2 + 2\gamma/(\gamma + 1)} \tilde{\sigma}_{ij} \), with rupture strain \( (r_a - r_m)/r_m \) independent of \( \tilde{\sigma}_{ij} \). Assuming \( \epsilon(\tilde{\sigma}_{ij}) \propto \sigma_{ij}^3 \), which is equivalent to taking the Young’s modulus \( Y \) to be uniform over the system [12], then the unit pressure \( \epsilon(\tilde{\sigma}_{ij})/\tilde{\sigma}_{ij}^3 \) is a constant. As a result, mechanical...
quantities with dimension of force per unit area become
scale invariant, for example the specific energy, the
pressure, the strength, and the elastic moduli. We parametrize
the interaction potential in Eq. (1) to describe the physical
properties of the hydration product C-S-H. We have in mind
mature C-S-H aggregates, because our simulation results
will be tested against experiment data at advanced stages of
insertion are in tension because of strong inter-
accommodate large particles [16]. The systems at the ter-
mination are in tension because of strong inter-
actions, and rate-dependent space filling. We examine
combined effects of relaxation under strong cohesive inter-
packing fraction produced through this procedure reflect the
convergence to a maximum value determined by the space
when the number of particles inside the simulation cell
measured directly for each location, while the local pack-
ing fraction
measured directly for each location, while the local pack-
ing fraction
measured directly for each location, while the local pack-
ing fraction
measured directly for each location, while the local pack-
ing fraction
measured directly for each location, while the local pack-
ing fraction
measured directly for each location, while the local pack-
ing fraction
measured directly for each location, while the local pack-
ing fraction
measured directly for each location, while the local pack-
ing fraction
measured directly for each location, while the local pack-
ing fraction
measured directly for each location, while the local pack-
ing fraction
measured directly for each location, while the local pack-
ing fraction
measured directly for each location, while the local pack-
ing fraction
measured directly for each location, while the local pack-
ing fraction
measured directly for each location, while the local pack-
ing fraction
measured directly for each location, while the local pack-
ing fraction
measured directly for each location, while the local pack-
ing fraction
measured directly for each location, while the local pack-
ing fraction
measured directly for each location, while the local pack-
ing fraction
measured directly for each location, while the local pack-
ing fraction
measured directly for each location, while the local pack-
ing fraction
measured directly for each location, while the local pack-
ing fraction
measured directly for each location, while the local pack-
ing fraction
measured directly for each location, while the local pack-
ing fraction
measured directly for each location, while the local pack-
ing fraction
measured directly for each location, while the local pack-
ing fraction
measured directly for each location, while the local pack-
ing fraction
measured directly for each location, while the local pack-
ing fraction
measured directly for each location, while the local pack-
ing fraction
measured directly for each location, while the local pack-
ing fraction
measured directly for each location, while the local pack-
ing fraction
measured directly for each location, while the local pack-
ing fraction
measured directly for each location, while the local pack-
ing fraction
measured directly for each location, while the local pack-
ing fraction
measured directly for each location, while the local pack-
ing fraction
measured directly for each location, while the local pack-
ing fraction
measured directly for each location, while the local pack-
ing fraction
measured directly for each location, while the local pack-
ing fraction
measured directly for each location, while the local pack-
ing fraction
measured directly for each location, while the local pack-

porosity C-S-H is
will be tested against experiment data at advanced stages of
Fig. 1(b) shows that the obtained packing fraction \( \phi_0 = \frac{\sum_{i=1}^{N} \frac{1}{6}(\sqrt{2}\sigma_i)^3}{V_0} \) starts at a value around random
close packing \(0.64\) for a monodisperse system and increases
nonlinearly with the polydispersity \(\delta\). The same
trend is seen in molecular dynamics simulations of jamming
polydisperse hard spheres [18]. This points to a certain
generality of how polydispersity affects packing fractions.
\( \phi_0 \) depends very weakly on the insertion rate \( R_p \) and therefore
on the shape factor \( \alpha \) of the PSD, within the range of
parameters explored here. This result differs from those
regarding hard spheres, where \( \phi \) can depend significantly
on \( \alpha \) [17]. We also find the specific cohesive energy
\( \sum U_{ij} / V_0 \) at zero pressure is weakly dependent on \( R_p \) and consequently on \( \alpha \). All this suggests that interactions and
relaxation to zero pressure play a central role in our study.
We will return to this discussion below.
We evaluate the elastic properties of the relaxed micro-
structures, by computing the full 4th order elastic tensor
using the stress fluctuation method [19], and assessing
mechanical rigidity through the corresponding acoustic
tensor [20]. From the bulk \( K \) and shear \( G \) moduli, we obtain the indentation modulus
\( M = 4G(3K + G)/(3K + 4G) \) (for a homogeneous isotropic material) [5].
Nanoindentation has been used to measure the mechanical
properties of C-S-H at the submicron scale [5]. The
experiments consisted of probing the sample surface at
different locations, with a needle of diameter \( \approx 100 \) nm.
The indentation modulus \( M \) and the hardness \( H \) are
measured directly for each location, while the local pack-
ing fraction \( \phi_0 \) is inferred by a self-consistent analysis.
Figure 2 shows the indentation modulus from our present

ambient pressure, we relax the microstructure by decreasing
the simulation cell dimensions via NPT ensemble, down to a volume \( V_0 \). Because our unit of pressure has a high value, \( e(\bar{r}_{ij})/\bar{r}_{ij}^3 = 0.204 \) GPa (from Ref. [14]), atmospheric pressure is effectively zero in our model.

The precipitation of C-S-H microstructures is simulated by
successively and randomly inserting particles into an initially
empty cubic periodic simulation cell. We use a Metropolis
algorithm with probability of insertion
\( P_{acc} = \min[1, e^{-\Delta U/(k_BT)}] \). \( \Delta U \) is the difference in interaction
energy after and before insertion, \( k_B \) is the Boltzmann constant,
and \( T = 298 \) K is the temperature [16]. Between
successive insertion attempts, a delay is introduced to allow
for structural relaxation in the NVT ensemble. The delay
consists of \( 1/R_p \) Monte Carlo displacements, with \( R_p \) being
the precipitation rate. The insertion procedure is terminated
when the number of particles inside the simulation cell
converges to a maximum value determined by the space
filling. Thus the particle configuration and corresponding
packing fraction produced through this procedure reflect the
combined effects of relaxation under strong cohesive inter-
actions, and rate-dependent space filling. We examine
monodisperse (\( \delta = 0 \)) and polydisperse C-S-H clusters up
to \( \delta = 0.47 \) (i.e., \( \sigma_M / \sigma_m = 10 \)). The range of particle size
considered lies between 1 and 10 nm. The total number of
Monte Carlo trials for the formation process ranges between
10^6 and 2 \times 10^{10}, the precipitation rate \( R_p \) between 1 and
10^{-6}, the simulation cell size between 6.8 \( \sigma_m \) and 40 \( \sigma_m \), and
the final number of particles between 300 and 12 000.

Results.—Figure 1(a) shows a typical configuration obtained at the end of our simulation of C-S-H microstructure
formation. Space filling progressively disfavors the inser-
tion of large particles, and the final particle size distribu-
tions (PSDs) deviate appreciably from the initial uniform
distribution. The resulting PSDs can be well described by
geometric distributions
\( p(\alpha) = \alpha \alpha^{n-1} / (\sigma_M^n - \sigma_m^n) \), also
known to be optimal for packing hard spheres [17]. We find
\( \alpha \) depends significantly on \( R_p \); namely, a small \( R_p \) leads to a
greater number of large particles. This seems physically
reasonable in that small \( R_p \) favors particle flocculation
between two successive insertions, creating wider voids to
accommodate large particles [16]. The systems at the ter-
mination of insertion are in tension because of strong inter-
particle attractions, and because structural rearrangements
are carried out under NVT condition. In order to compare
our results with experiments on mature C-S-H specimens at

FIG. 1 (color online). (a) Snapshot of a simulated nanostruc-
ture with \( \delta = 0.47 \). The color code highlights the particle sizes
(from small dark-red to large light-green ones). (b) Packing
fraction \( \phi_0 \) as a function of polydispersity \( \delta \); the shaded region
corresponds to the range of jamming volume fractions for
polydisperse hard spheres from Ref. [18]. Our results are aver-
age over 3–4 samples [16]. Error bars are within the marker
symbol sizes. The lines are to guide the eye.
study at five packing fractions and their corresponding $\delta$ values. Also shown are the experimental data on the C-S-H phase in a white cement paste specimen [5,11].

The experiments indicated that within the same sample of C-S-H, the packing fraction $\phi_0$ varied significantly with location. $\phi_0$ ranges between 0.5 and 1, clustering between 0.6 and 0.8. $M$ increases linearly with $\phi_0$, and extrapolates to zero at $\phi_0 \approx 0.5$. We regard Fig. 2 as a reasonable validation of our attempt to describe the correlation between elastic rigidity and the packing fraction of C-S-H. Figure 1(b) provides the additional insight that in the present study a greater packing fraction, and correspondingly higher strength (see Fig. 2), entails larger polydispersity. This suggests a high degree of structural heterogeneity already at the submicron scale. It also indicates that the large fluctuations in local densities observed experimentally could be arising from large spatial variations of polydispersity of the C-S-H aggregates. Furthermore, because of size variation of the effective interactions, relatively soft domains can exist within stiffer regions. Such soft domains would consist of smaller particles, which are much more liable to local rearrangements, while the strongly cohesive large particles constitute the high stiffness backbone of the microstructure.

Figure 3(a) shows pressure-strain curves obtained by isotropic compression of the systems: from the reference state ($P = 0$) to a volume strain of $\varepsilon_{\text{vol}} = -10\%$ ($P > 0$), and then reversing back the strain loading to reach $P = 0$. All the curves show a significant hysteresis, indicating a plastic behavior which we consider related with the creep observed in nanoindentation experiments [9]. The analysis of local response, performed on a subsystem and shown in Fig. 3(b), indicates that such plastic behavior can be associated with local irreversible events, abrupt intermittent yielding (strain changes). These may be seen as the analogue of discrete deformations characteristic of nanoscale strain localization in atomistic simulations [21]. Experimentally, serrated flows in metallic glasses observed by in situ atomic emission monitoring have been linked to the initiation of shear bands [22]. We also observe that polydispersity tends to suppress serration behavior and, therefore, strain localization, which is consistent with reaching higher stresses at the same compression strain. An explanation is that the less mobile large particles in polydisperse systems can act as hard inclusions blocking the avalanche of irreversible displacements. We therefore expect that the behavior under large deformations should be affected by the PSD even at a fixed packing fraction, differently from the elastic moduli which we observe depend only on the packing fraction.

Our simple model brings out a physical picture of the structural and mechanical complexity of the C-S-H, which can help to resolve apparently contradicting observations. The microstructure of C-S-H displays indeed different characteristics when probed by different experimental techniques. Small-angle neutron scattering suggests C-S-H has a continuous gel-like structure with long range spatial correlations [8]. Various experimental techniques indicate the presence of nanocrystals with 1–10 nm size, with a disordered mesoscale organization [3,8,23,24]. On the other hand, nanoindentation, sampling spatial regions of order 100 nm, detects rather granular features of this solid [5,9]. It is conceivable that the three interpretations are parts of the same picture and, in fact, all these structural characteristics are resolved in the microstructure seen in high-resolution transmission electron microscopy images [24,25]. This multdomain character of the C-S-H microstructure is reflected in our model, where the attractive strength $\varepsilon$ scales as the particle volume $\sigma^2$. Polydispersity hence can account for the presence of harder nanocrystalline regions embedded into a disordered softer matrix with similar chemical composition. Weak interactions in the matrix of small particles allow thermal motions to be important, which may give rise to the features of a relatively soft gel. On the other hand, the highly cohesive network of large inclusions causes the granular type of mechanical response.

Returning to the correlation between the packing fraction $\phi_0$ and polydispersity, in our model we included attractive interactions, structural relaxation, and a finite...
precipitation rate \( R_p \), which go beyond packing of hard spheres. We have shown the resulting PSDs depend sensitively on \( R_p \), although \( \phi_0 \) and specific cohesive energy do not. Our interpretation is that the attractive interactions and the relaxation to zero pressure improve the efficiency and robustness of the packing, consistent also with the packing fraction of hard spheres with a potential-based protocol [10]. In fact our algorithm always approaches the random close packing for monodisperse systems [see Fig. 1(b)]. This synergistic effect of statics and dynamics on packing of cohesive media can be subtle and novel.

Several aspects of this work can benefit from refinements and extensions. We have thus far assumed the C-S-H particles are spherical but recent experiments suggest a platelet shape [26]. Ellipsoidal shapes can lead to a higher packing fraction, because of a larger number of possible particle contacts [27], but the coupled effect of shape and polydispersity remains to be studied. We anticipate the relation between the packing fraction and elastic properties (see Fig. 2) to depend more strongly on polydispersity than on particle shape, because of the \( e(\sigma) \sim \sigma^3 \) scaling. Nevertheless, significant particle shape effects may emerge at large strain and with respect to failure mechanisms. Heterogeneous growth from unhydrated cement grain surfaces and a variable ionic solution may contribute to the experimentally measured spatial variety of the C-S-H packing fraction [28], and can also be considered in our model [16]. Finally, we note that cement setting belongs to a class of materials aging phenomena associated with slowly evolving structures. Irreversible deformation and viscoelastic response are manifestations of metastable equilibrium states that our discrete modeling approach can investigate systematically. Dynamical features such as glass rheology, creep deformation, and stress corrosion cracking [29,30], point to a new physical perspective for a broad appreciation of cement research.

This work is supported by Schlumberger (SDR Cambridge, U.S./SRPC Clamart, France) and by the CSHub at MIT. E. D. G. is supported by the SNSF (Grant No. PP00P2_126483/1).

[14] \( \epsilon_{ij} \) is obtained from \( Y \) with a harmonic approximation, i.e., considering \( d^2U_{ij}/dr_{ij}^2 \) for \( r_{ij} = r_m \) equal to \( Y \delta_{ij} \).
[15] The dimensionless temperature \( T' = k_B T / e(\sigma_{ij}) \), at \( T = 298 \, K \), is \( T'(\sigma_{ij} = 1 \, nm) = 2.25 \times 10^{-2} \).
[19] J. F. Lutsko, J. Appl. Phys. 65, 2991 (1989); We also cross-check the values of the bulk \( K \) and shear \( G \) moduli using a finite strain approach, obtaining good agreement.
[20] J. A. Ortega, F.-J. Ulm, and Y. Abousleiman, Geophys. Res. Lett. 74, D65 (2009); The largest eigenvalue of the acoustic tensor is the longitudinal wave velocity. For our systems it is \( \sim \)constant in each direction, with negligible polarization, indicating isotropy.
[29] Stress corrosion cracking, typical of metals, is analogous to coupled chemical degradation—fracture in cement.