Masoero E, Del Gado E, Pellenq RJM, Yip S, Ulm F-J.

[Nano-scale mechanics of colloidal C--S--H gels.](#)

Soft Matter 2014, 10(3), 491-499.

Copyright:

This is the authors' accepted manuscript of an article that was first published in its final definitive form by Royal Society of Chemistry, 2014.

DOI link to article:

<http://dx.doi.org/10.1039/C3SM51815A>

Date deposited:

28/04/2016

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Nano-scale mechanics of colloidal C–S–H gels

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Received Xth XXXXXXXXXX 20XX, Accepted Xth XXXXXXXXXX 20XX

First published on the web Xth XXXXXXXXXX 200X

DOI: 10.1039/b000000x

Gels of Calcium-Silicate-Hydrates (C–S–H) are the glue that is largely responsible of the mechanical properties of cement. Despite their practical relevance, their nano-scale structure and mechanics are still mainly unexplored, because of the difficulties in characterizing them in a complex material like cement. We propose a colloidal model to investigate the gel mechanics emerging in the critical range of length-scales from several tens to hundreds of nanometers. We show that the size polydispersity of the hydrates and size-dependent effective interactions can explain the mechanical heterogeneities detected in nano-indentation experiments. We also show how these features control the arising of irreversible structural rearrangements under deformation, which are good candidates as nano-scale mechanisms underlying mechanical aging and slow structural relaxation in the gels.

1 Introduction

Calcium-silicate hydrates (C–S–H) form inorganic hydrogels with a variety of complex nano-scale structures^{1–4}, depending on the external chemical and physical environment. These gels are the main binder phase of ordinary cements, determining to a large extent the properties of the most widely used material on Earth. The C–S–H phase in cement forms upon chemical reaction between the fine clinker powder (containing calcium silicates) and water, and precipitates from the supersaturated pore solution rich in calcium and silicon ions. Controlling the complex chemo-mechanical processes that underlie the precipitation of the hydrates and the development of the cohesive gel is a strenuous undertaking. In the experimental systems it has been so far impossible to separate the different basic mechanisms from their combined effects. In particular this would require a deep understanding, far from being reached, of transport and aggregation phenomena that are also typical of other colloidal and soft-matter systems. In the case of cements, such phenomena take place in far-from-equilibrium conditions that are closely intertwined with the chemical evolution of the environment. Although several aspects of this chemical evolution, from the dissolution of the clinker to the precipitation of C–S–H, have been systemati-

cally investigated^{5–7}, the development of the physical properties of the gel is still mainly unexplored. Hence, for example, it is still fundamentally not known which features of the nano-scale structure of the gel are important for the overall mechanics of the material. Experiments have recently shown that the C–S–H dense gels in hardened cement paste, i.e. at the end of hydration, still display an inexorably slow mechanical aging and indicated that this affects the material performance up to the level of concrete structures^{8,9}. Specific structural features of the C–S–H gels, developed under the non-equilibrium conditions of hydration, might control mechanical aging and, once identified, could be used as levers to control also other aspects of the non-linear mechanical response of the material. Achieving such understanding could lead to a real breakthrough on how to design new *green* formulations of cement without sacrificing the mechanical performance.

In C–S–H gels the range of length-scales from several tens to hundreds of nanometers, typical of soft matter systems, is particularly crucial. The structural heterogeneity and lack of long-range order that clearly arise over these length-scales ultimately determine the mechanical response¹⁰. This range of length-scales has been hardly addressed by modeling and computational studies that, so far, have been mostly focused on sub-nanometer scales or to the other end on the micrometer-scale structure of the C–S–H phase^{11–14}. With the aim of investigating these intermediate lengthscales, we have recently proposed a new colloidal model for the C–S–H gels¹⁵. We described the dense C–S–H gel as a polydisperse assembly of nano-scale colloidal (spherical) particles that interact via a simple attractive potential well. The attraction strength and width were set using information from experiments and atomistic simulations¹¹. We employed a Monte Carlo procedure to generate disordered assemblies of

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such particles. The results of our numerical mechanical tests showed that the indentation moduli measured in experiment can be ascribed to large size polydispersities of the hydrates in the gels¹⁵, an information that is not accessible experimentally. These first results open a whole set of new questions. In particular, TEM images and neutron scattering experiments^{6,16,17} indicate rather anisotropic shapes and contact areas with finite extent, which is likely to significantly change the mechanics of the assemblies. Although here we do not address the anisotropy of the particles directly, we consider the effect of finite contact areas by introducing size dependent interactions in our model. We then investigate the nano-scale mechanics of the C–S–H gels obtained with different degrees of polydispersity. The results of our mechanical tests indicate an excellent agreement with the elastic moduli of the C–S–H gel as measured by nanoindentation experiments. Starting from this, we analyze the role of polydispersity in the onset of plastic events and we prove that structural heterogeneities of the type considered here can be crucial in C–S–H gels.

The paper is organized as follows: in Section 2 we describe the model and the numerical simulations. In Section 3 we perform numerical studies of the mechanical response of the model C–S–H gels under small and large deformations. In particular, after discussing the elastic behavior in Section 3.1, we analyze irreversible processes underlying the onset of non-linear response under shear in Section 3.2. In Section 3.3 we show that the irreversible processes are directly related to stress drops and local non-affine rearrangements, and that size polydispersity plays an important role. Conclusions and an outlook for this work are discussed in Section 4.

2 C-S-H gel structures: polydispersity, interactions, and generation algorithm

We consider that, by the end of the hydration process, a dense cohesive C–S–H gel is formed and that its sub-micrometer structure can be well represented by a disordered assembly of colloidal polydisperse hydrates. This accounts for attractive effective interactions that introduce spatial correlations as well as correlations between sizes and positions of the particles in the structure. Hence we produce disordered sub-micrometer structures using a Monte Carlo space filling algorithm that minimizes the interaction energy¹⁵.

For the effective interactions between the colloidal particles we use a simple well potential:

$$U_{ij}(r_{ij}) = 4 \varepsilon(\sigma_i, \sigma_j) \left[\left(\frac{\bar{\sigma}_{ij}}{r_{ij}} \right)^{2\alpha} - \left(\frac{\bar{\sigma}_{ij}}{r_{ij}} \right)^\alpha \right]. \quad (1)$$

where σ_i and σ_j are the diameters of particles i and j , r_{ij} is their relative distance, and $\varepsilon(\sigma_i, \sigma_j)$ is the well depth between

them. α controls how narrow the potential well is, and $\bar{\sigma}_{ij} = (\sigma_i + \sigma_j)/2$.

The internal, sub-nanometric structure of C–S–H hydrates is known to be anisotropic, as it is characterized by silicate chains and calcium oxide layers with water layers in the interlaminar spaces between them^{18–20}. In the crystalline form (tobermorite), the silicate chains are continuous. By contrast, the additional calcium that is usually present in the C–S–H in cement causes distortions of the layers and trimming of the silicate chains¹¹. This complex molecular structure translates into effective interactions among hydrates in the C–S–H gels which have been the subject of an intense debate in the last few years, and are still under investigation^{21,22}. In absence of deeper understanding, we assume that anisotropy is lost, on average, over distances of few nanometers, due to random orientation of the layers. We therefore consider only central forces, although more complicated effective interactions can be certainly implemented in our approach and will be the subject of future studies. We consider that the hydrates get strongly bonded in the gel through the calcium-silicate layers and therefore the interaction strength must depend, among other factors, on the contact area between pairs of particles, viz. the size of the interface between them. We account for this by considering a size dependent interaction strength $\varepsilon(\sigma_i, \sigma_j)$. We compute the prefactor by considering the two hydrates in contact as two springs in series, which leads to $\varepsilon(\sigma_i, \sigma_j) \simeq A_0 \beta_{ij} \bar{\sigma}_{ij}^3$. A_0 is a factor proportional to the Young modulus of a hydrate (assumed equal for the two particles). $\beta_{ij} = \sigma_i \sigma_j / \bar{\sigma}_{ij}^2$ is a correction term that arises from the serial arrangement, and was not included in the previous version of the interaction potential in ref.¹⁵. It is interesting to note that a similar type of scaling $\varepsilon(\sigma_i, \sigma_j) \propto \bar{\sigma}_{ij}^3$ would emerge from a Hertz type of contact²³ between particles i and j , with the difference that the Hertz contact model accounts only for repulsion while our formulation includes cohesion as well.

The energy scale for the cohesion between particles i and j , i.e. the prefactor A_0 in $\varepsilon(\sigma_i, \sigma_j)$, and α in Eq. 1 can be set on the basis of properties measured from atomistic simulations^{12,24}. From the shear strain at rupture $\gamma_u \approx 10\%$ measured for a stack of silicate layers we can estimate an equivalent uniaxial strain at tensile rupture $\varepsilon_u = (\sqrt{\gamma_u^2 + 2\gamma_u + 2} - \sqrt{2})/\sqrt{2} \simeq 5\%$ (viz. the tensile principal strain associated with a pure shear strain γ_u). The attractive force from Eq. 1 is null at a distance $r_m = \sqrt[3]{2} \bar{\sigma}_{ij}$: from this, for simplicity we can redefine the diameter of particle i as $\sigma_{0,i} = \sqrt[3]{2} \sigma_i$. The maximum tensile force is attained at a distance $r_u = \sqrt[3]{\frac{4\alpha+2}{\alpha+1}} \bar{\sigma}_{ij}$, corresponding to a strain $\varepsilon_u = (r_u - r_m)/r_m$, and, by choosing $\alpha = 14$, this gives $\varepsilon_u = 4.82\%$, in reasonably good agreement with the indications from atomistic simulations. A relatively narrow potential well, as given by $\alpha = 14$, is also con-

Fig. 1 Snapshots from a simulation to generate a model C-S-H structure extracting particles from a reservoir with polydispersity $\delta = 0.38$. The color code indicates the particle size that, in our model, is indicative also of the strength of cohesion. Due to space filling, as the simulation advances the small particles increase in number compared to the large ones.

sistent with AFM measurements²². If we assume that the cohesive strength between our colloidal particles is basically the same as the cohesion between calcium-silicate layers within each hydrate, we can set the energy scale[†] using the value of the Young modulus $Y = 63.6$ GPa obtained from atomistic simulations performed on calcium-silicate-hydrates of a few nanometers²⁴. This corresponds to interaction strengths ranging between $1000k_B T$ and $1.5 \cdot 10^6 k_B T$ ($T = 300$ K), respectively for the smallest ($\sigma = 3$ nm) and largest ($\sigma = 35$ nm) particle sizes that we consider here[†].

We start from an initially empty cubic simulation box of linear size L in contact with an infinite reservoir of C-S-H nanoparticles. The linear size σ of the particles in the reservoir follows a uniform distribution between a minimum σ_m and a maximum σ_M value. The standard deviation δ of this distribution in units of $1/2(\sigma_M + \sigma_m)$ defines the polydispersity. A particle size is randomly extracted from the reservoir and an insertion at a random location in the simulation box is tried. The insertion is accepted with probability $P_{creat} = \exp(-\Delta U/k_B T)$, where k_B is the Boltzmann constant and ΔU is the difference in total interaction energy caused by the trial insertion. We also allow for particle displacements within the box, trying $D_p N$ Metropolis Monte Carlo moves in the NVT ensemble after every trial insertion. N is the number of particles in the box, which increases with the simulation time, and D_p is an arbitrary “delay” parameter, qualitatively inverse to a precipitation rate. The algorithm proceeds until N approaches a constant maximum value, i.e. space is filled. A typical sequence of snapshots is shown in Fig. 1. In all simulations discussed here, the delay parameter D_p is kept fixed to

10^{-2} . Four different polydispersities are considered (see Table 1) and we use between 10^7 and $2 \cdot 10^9$ Monte Carlo steps, depending on the simulation.

We compute an approximate solid volume fraction, or packing fraction $\phi = \sum_i \pi/6 \sigma_{0,i}^3 / L^3$, where we use the particle diameter defined previously $\sigma_{0,i} = \sqrt[4]{2} \sigma_i$. Fig. 3 shows that, as expected, a better packing is achieved at high polydispersity¹⁵. As space filling proceeds, inserting large particles becomes unlikely while smaller particles can still fit (see Fig. 1). This causes the final particle size distribution to differ significantly from the uniform distribution in the reservoir. The final particle size distributions are geometric^{15,25}, as shown in Fig. 4.

Fig. 2 Interaction potential for pairs of particles with sizes σ_i and σ_j . For comparison, the dashed lines show repulsive terms obtained from the Hertz contact model with modulus $M = 65$ GPa.

[†] The serial arrangement in Fig. 2, with $Y\pi\left(\frac{\sigma_{0,i}}{2}\right)^2 / \frac{\sigma_{0,i}}{2}$ being the stiffness of the spring associated with the i^{th} particle, leads to $\varepsilon(\sigma_i, \sigma_j) = 0.002324 Y \beta_{ij}(\sigma_i, \sigma_j) \bar{\sigma}_{ij}^3$.

Table 1 Explored polydispersities δ , corresponding minimum and maximum particle sizes (σ_m and σ_M), range of explored linear size L of the cubic simulation box, and range of number of particles N obtained at the end of the space filling process.

δ	σ_m (nm)	σ_M (nm)	L (nm)	N
0	5	5	40 – 60	504 – 6968
0.19	3.5	7	50 – 70	1495 – 4087
0.38	3	15	42 – 90	907 – 7112
0.47	3.5	35	92 – 190	3731 – 17670

Fig. 3 Effect of polydispersity δ on the packing fraction ϕ . We show results for systems both just after their formation and after the subsequent relaxation to zero stress or pressure, which generally reduces the volume and therefore increases ϕ . The shaded region refers to jammed hard sphere packings²⁶.

3 Mechanical properties of the polydisperse C-S-H structures

In this section we investigate the mechanical properties of the model C-S-H structures obtained from the simulations. The structures at the end of the space filling are all under negative pressure, i.e. tensile (virial) normal stresses²⁷, due to attractive interactions and periodic boundary conditions. To mimic more realistic ambient conditions we relax the model structures to zero stress using the isotension isothermal NtT ensemble^{28,29}. Fig. 3 shows that the packing fraction increases for all δ after relaxation and the results are consistent with those in¹⁵, as well as with the packing fractions of jammed, polydisperse hard spheres²⁶. The new features of the potential implemented here to better capture the contact area between particles do not seem to affect significantly the packing, whereas they do have an effect on the mechanical properties.

* We prefer the NtT over the isobaric NPT ensemble because relaxing all six stress components independently toward zero provides a reference configuration that is appropriate to any type of subsequent test conditions, e.g. volumetric, deviatoric or uniaxial.

Fig. 4 Dimensionless particle size σ^* distributions. $P(\sigma^*)$ is the cumulative probability. The solid lines are fits assuming a geometric size distribution, with shape parameters^{15,25} -4.2, -3.25, and -2.9 respectively for the cases with $\delta = 0.19, 0.38$, and 0.47 .

3.1 Elastic properties at zero stress

We characterize the elastic properties of the model C-S-H structures in terms of the tensor of elasticity. The tensor is computed keeping fixed the simulation box after equilibration to zero stress, and using the stress fluctuation method³⁰. According to this method the tensor of elasticity $[C]$ (a 6×6 matrix in Voigt notation) is decomposed into a configurational contribution related to the second derivatives of the potential in Eq. 1, and a stress fluctuation component that includes the temperature. For an isotropic material, the only non-zero values of C_{ij} are for $i, j \leq 3$ and for $i = j$. Table 2 shows a typical elastic tensor for one of our monodisperse configurations: there are some small deviations from the isotropic case, probably due to the finite size and to the fact that NtT relaxation leads to stresses that, although very small, are not exactly zero. Nevertheless, the deviations from the isotropic case do not follow a clear trend and are small enough to assume that isotropy holds for the elastic properties of the systems. Polydispersity

Table 2 Tensor of elastic constants (in GPa units) for the monodisperse system with $N = 504$, in Voigt notation. The tensor is symmetric and the lower half is not shown for better readability. The terms in gray should be zero for isotropic materials.

C_{ij}	$i = 1$	2	3	4	5	6
j=1	30.92	17.61	20.99	-0.15	-0.18	0.58
2		31.21	18.82	1.25	-0.86	0.35
3			30.87	-1.34	0.93	0.41
4				6.87	-0.53	0.02
5					7.18	0.26
6						7.25

Fig. 5 Indentation moduli vs packing fraction. Comparison between our simulations and nano-indentation experiments¹¹.

increases the finite terms of [C] (darker in Table 2), corresponding to higher stiffnesses, certainly due the higher packing fractions and different stress distribution attained. For an isotropic material, we can use the Voigt formulas to compute the bulk (K) and shear (G) moduli from the components of [C] and obtain the indentation modulus M ^{8,31}:

$$M = 4G \frac{3K + G}{3K + 4G} \quad (2)$$

The indentation modulus is proportional to the stiffness of contact, i.e. the slope during unloading of the load-penetration curve obtained from indentation tests⁸. Being the diameter of a nano-indenter's tip in the order of few hundreds of nanometers, the indentation modulus allows a direct comparison between our simulation results and nano-indentation experiments on C-S-H gels. In Fig. 5 we plot the indentation moduli computed for our model structures as a function of their packing fractions. Experimental data for a white cement paste¹¹ are also shown and indicate an excellent agreement. The present study improves significantly the agreement with the experimental results compared to a previous work¹⁵, where the contact area between particles was approximated as $\bar{\sigma}_{ij}^2$ in the effective interaction potential (cf. Eq. 1). This led to an overestimation of indentation moduli in ref.¹⁵, although the linear trend with ϕ was preserved.

3.2 Shear deformations and irreversible rearrangements

Large deformations cause a nontrivial evolution of internal stresses in the C-S-H gels. In order to investigate this, we subjected the structures obtained for different polydispersity to a series of pure shear strain increments $\Delta\epsilon_{xz} = \Delta\epsilon_{zx} = 0.005$. Each strain increment is followed by $5 \times 10^7 - 3 \times 10^8$ Monte Carlo trial displacements performed in the NhT ensemble,

Fig. 6 Pure shear stress τ - strain γ tests for systems with different polydispersity δ (and packing fraction ϕ , which increases with δ , as shown in Fig. 3). The inset shows the evolution of the shear elastic modulus G during the tests.

i.e. keeping the simulation box fixed, after which we compute the shear stress τ_{xz} . In Fig. 6 we plot the shear stress τ (i.e., τ_{xz} averaged over statistically independent samples) as a function of the cumulative strain $\gamma = 2\sum\Delta\epsilon_{xz}$, for systems with different polydispersity. The data show that small cumulative strains ($\gamma \leq 0.03$) are accompanied by a first rapid increase of stresses in the material. At larger γ all systems undergo yielding at a stress level that increases significantly upon increasing the polydispersity. The yielding stress is a measure of strength, and nanoindentation experiments⁸ confirm that the strength of the C-S-H (quantified by the hardness) increases with its packing density, i.e. with the polydispersity in our model (see Fig. 3). The inset of Fig. 6 shows the shear moduli G evaluated at different γ from the elastic tensor (see Section 3.1): starting from values in agreement with the ones computed from the fluctuations at $\gamma = 0$, the data start to display deviations that suggest mechanical instability³². The deviations seem to increase upon increasing the polydispersity, but a more quantitative analysis would require a dedicated study[‡].

The response to the cumulative shear strain is accompanied by a change in the pressure, as shown in Fig. 7. This indicates a coupling between the deviatoric and the hydrostatic components of the stress. In particular, the monodisperse and weakly polydisperse systems display a negative pressure when the strain γ is low, i.e., they would contract under shear if the volume were allowed to relax in isobaric conditions at $p = 0$. By contrast, higher levels of stress in the monodis-

[‡] It is worth reminding that the highly polydisperse systems may be more significantly affected by finite size effects.

Fig. 7 Pressure p built up during the shear strain γ tests in Fig. 6, for systems with different polydispersity δ (and packing fraction ϕ , which increases with δ , as shown in Fig. 3). The inset shows the evolution of the anisotropy modulus $K_{p\gamma}$ during the tests.

perse and weakly polydisperse systems induce an increasingly positive pressure: a tendency to dilate that is strongly reminiscent of dilation typical of granular, athermal systems³³. Interestingly, the highly polydisperse systems ($\delta = 0.38$, corresponding to the highest volume fraction) display positive pressure, i.e. a tendency to dilate, at all levels of applied strain). The correlations between τ and p correspond to an increase of the non-zero terms C_{15} , C_{25} , and C_{35} in the elastic tensor (e.g. in Table 2) and could therefore suggest a stress-induced anisotropy³⁴. We have quantified this buildup of anisotropy by computing a modulus $K_{p\gamma} = -(C_{15} + C_{25} + C_{35})/6$, obtained from $p = -1/3(C_{15} + C_{25} + C_{35})\epsilon_{xz}$. $K_{p\gamma}$ is plotted against γ in the inset of Fig. 7 and grows indeed with γ (for $\gamma \leq 0.1$) and with increasing polydispersity.

In order to distinguish between the reversible and the irreversible parts of the deformation, each configuration corresponding to (γ, τ) pairs in Fig. 6 is then relaxed back to $\tau = 0$. This is accomplished varying the strain components $\epsilon_{xz} = \epsilon_{zx}$ of the simulation box in mixed NHT-NtT ensemble. In general the residual shear strain γ_{res} , after τ is relaxed back to zero, is not null, as it should instead be in the case of a fully elastic response. Fig. 8 shows that γ_{res} is continuously growing as a function of the shear strain γ applied before relaxation. The increase of γ_{res} with γ becomes more pronounced and approximately linear for strains $\gamma > 0.02$, for the systems with lower polydispersity, $\delta = 0$ and $\delta = 0.19$. For the more polydisperse systems, with $\delta = 0.38$, this occurs at larger strain $\gamma > 0.05$.

These results indicate overall that the dense C-S-H gels display a non linear response characterized by yielding, mechanical instability, and structure recoveries, all accompanied

by the development of anisotropy and probably associated to irreversible dynamical processes. This is also supported by the

Fig. 8 Irreversible deformations: residual shear strain after relaxation back to zero shear stress $\tau = 0$ of systems previously loaded to γ (see Fig. 6). The systems have different polydispersity δ (and packing fraction ϕ , which increases with δ , as shown in Fig. 3). The inset shows the change of interaction energy after relaxation ΔU_{res} induced by the deformation γ , and divided by the absolute value original of interaction energy of the systems at zero strain and stress ($\gamma = 0, \tau = 0$). Averages and standard deviations were computed from 13 statistically equivalent samples for $\delta = 0$, 6 samples for $\delta = 0.19$, and from two samples for $\delta = 0.38$.

data in the inset of Fig. 8, which shows the internal energy U_{res} of the systems relaxed from γ back to $\tau = 0$. U_0 is the total internal energy of the original C-S-H structures at zero stress before the shear test, and $\Delta U_{res} = U_{res} - U_0$. The data indicate that the applied strain allows attaining a better stability upon relaxing the stresses, with a residual internal energy that is always lower than the one of the initial configurations. For the monodisperse and weakly polydisperse systems this is consistent with the development of pressure in Fig. 7 and indicate a progressive compaction of the structures. Nevertheless, it is interesting to notice that also the highly polydisperse systems become more stable under shear, in spite of their tendency to dilate indicated by the positive pressure in Fig. 7. Finally, Fig. 7 indicates that despite the accumulated γ_{res} is comparable for all systems irrespective of their polydispersity δ , the change in potential energy is much more significant in the monodisperse and weakly polydisperse systems, which is probably due to their lower packing fraction ϕ (see Fig. 3).

3.3 Stress drops and local analysis of the non-affine displacements

To further investigate the irreversible dynamical processes that may underlie the mechanical instability associated to the yielding, we have analyzed the load curve of each sample separately. Fig. 9 shows a portion of the stress-strain curve of a monodisperse system with $N = 508$ and the accumulation of irreversible deformations γ_{res} [§]. The curve displays sudden stress drops that are more dramatic compared to those in Fig. 6, where averages were taken over different samples. One can immediately recognize that these drops are directly correlated to a step increase of residual strains γ_{res} (upon relaxing the deformed structure back to $\tau = 0$), although not all stress drops are accompanied by irreversibility (quantified by γ_{res}). Before the first stress drop occurs ($\gamma < 0.01$ for the sample in Fig. 9) the system response is linear elastic, as indicated by its ability to completely relax the internal stresses developed under deformation without residual strains. We also observed sudden drops of pressure towards negative values in correspondence to the drops of shear stress. We have tested the possibility that, for the monodisperse systems, the drops of stress accompanied by a negative pressure and an overall decrease of interaction energy at rest (see the inset of Fig. 8) may be due to local crystallization. This seems not to be the case here, because we observe that in most of the cases the fraction of particles with local crystalline order decreases during the shear test. This absence of crystallization in the monodisperse systems is consistent with the comparable behaviors of the monodisperse $\delta = 0$ and the weakly polydisperse systems $\delta = 0.19$ shown in Figs. 6, 7, and 8, which have similar packing fractions^{35–38} include the constant-volume shear protocol that we employed, as opposed to a constant pressure one, and the narrow interaction potential (see Section 2).

For each strain increment, Fig. 9 shows also the average magnitude of the non-affine displacement vectors, averaged over all the particles in the box $\langle \eta_{na} \rangle$, and the corresponding standard deviations $\sigma(\eta_{na})$. Non-affine displacements always accompany the deformations of disordered solids, also within the elastic regime, but during irreversible events they are normally larger^{39–41}. Fig. 9 shows in fact that the magnitude of the average non-affine displacement $\langle \eta_{na} \rangle$ is dominated by such irreversible particle rearrangements. Furthermore, it is interesting to notice that the stress drops not corresponding to an irreversible displacement are instead captured by the ratio between the standard deviation of η_{na} and its average. This suggests that such events are more “local”, i.e. they involve a

Fig. 9 Top: shear stress-strain curve and corresponding accumulation of irreversible strain γ_{res} after relaxation back to $\tau = 0$, for the monodisperse systems with $N = 508$. Bottom: magnitude of the non-affine displacement vector averaged over the particles $\langle \eta_{na} \rangle$ and corresponding standard deviation $\sigma(\eta_{na})$, associated with each strain increment.

smaller number of particles (the standard deviation is in fact more sensitive to the tail of the distribution of η_{na}). Local events that cause instability but are not accompanied by irreversibility might be a signature of local mechanisms of elastic Eulerian instability⁴².

In order to study the effect of the polydispersity on the non-affine displacements, in Fig. 10 we plot the accumulated $\langle \eta_{na} \rangle$ (averaged over 2–4 statistically independent samples) for systems with different polydispersities, as a function of the cumulated shear strain. Fig. 10 shows that the total non-affine displacements increase continuously after yielding, when irreversible dynamical processes govern the non-linear response. The systems with high polydispersity $\delta = 0.38$ seem to accumulate an amount of non-affine displacement comparable to that of weakly polydisperse ($\delta = 0.19$) and monodisperse ($\delta = 0$) systems. Therefore the accumulated average non-affine displacement does not reflect the smaller tendency of highly polydisperse systems to develop irreversibility, as shown instead by the inset of Fig. 8. **EMA: here you suggested to change the last sentence to: “Nevertheless, highly polydis-**

[§] For illustrative purposes in Fig. 6, among all the systems that we analyzed, we decided to refer to a monodisperse one with very small size. The reason is that the effect of local irreversible deformation events on systems-level quantities, e.g. the magnitude of stress drops and the increase of γ_{res} , is more pronounced in small, monodisperse systems.

Fig. 10 Total non affine displacements accumulated during the shear tests, between $\gamma = 0$ and γ . Averages and standard deviations were computed from four statistically equivalent samples for $\delta = 0$ and $\delta = 0.19$, and from two samples for $\delta = 0.38$.

perse systems have a weaker tendency to develop irreversibility, as shown by the inset of Fig. 8).” I’m ok with it, but I’d like you to appreciate that the original point of my sentence was to point out that the average eta is not a good enough indicator, because it is unable to capture the weaker tendency of polydisperse systems to develop irreversibility (inset of Fig. 8). A better understanding will come from Fig 11 and 12, where we show the eta per particle as a function of the particle sizes. What do you think?

To further and more directly investigate the role of polydispersity, in Fig. 11 we plot the magnitude of non-affine displacements as a function of the particle diameters. Small particles experience larger non affine displacements during an irreversible event, which indicates that they govern the accumulation of irreversibility. This concentration of non-affine displacements in the small particles is enhanced upon increasing the polydispersity, suggesting that large particles may behave as inclusions that hinder the development of deformations within a matrix composed of smaller particles. Small particles are indeed orders of magnitude more abundant than large ones, as shown in Fig. 4. In order to test this hypothesis, we have computed the average non-affine displacements accumulated as a function of the applied strain (analogous to Fig. 10) for subsets of particles. The subsets are generated considering only the particles whose size σ_i satisfies the condition $\sigma_i \geq \sigma_m + b(\sigma_M - \sigma_m)$, where σ_m and σ_M are the smallest and largest size possible for the specified polydispersity δ (see Table 1). In Fig. 12 we consider two samples, one with low and one with high polydispersities. We show the non-affine displacement accumulated by the largest particle only,

Fig. 11 Non affine displacement as a function of particle diameter, during an irreversible event.

as well as the one averaged over three subsets of particles corresponding to $b = 0$ (all the particles, as in Fig. 10), $b = 0.25$, and $b = 0.75$. Similarly to Fig. 11, one can appreciate that the largest particles are characterized by relatively smaller non-affine displacements. In addition to that, for low cumulative strains all particles appear to contribute similarly to the non-affine displacements, while for relatively higher γ the contribution of the largest particles drops significantly. This effect becomes more dramatic upon increasing the polydispersity. In particular, for the higher polydispersity considered here, the regime in which the strain is localized in regions densely populated by small particles seems to coincide with the onset of the non-linear response ($\gamma \simeq 0.05$). This supports our interpretation that large particles behave as inclusions after the onset of yielding, and that they need to be excluded from the subsequent plastic flow. The emerging physical picture is that high polydispersity, which allows to achieve higher packing fractions, may hinder the non-affine rearrangements of small particles that go around and exclude large ones. This can result in a broadening of the elastic regime in Fig. 8 (e.g., until $\gamma \simeq 0.05$ instead of $\gamma \simeq 0.02$ detected for the systems with low and no polydispersity), until the largest particles are *unlocked* and the system yields (Fig. 12).

4 Conclusions

In this work we have developed new understanding of the mechanical response of dense, out-of-equilibrium assemblies of interacting, polydisperse, colloidal particles, with the aim of linking the observed behaviors to the mechanics of the C–S–H gels in cement pastes. Our colloidal approach allows to investigate the range of length-scales between nanometers and micrometers that is still largely not understood in this class of materials, although it is crucial for the development of struc-

Fig. 12 Average non affine displacements for particles with size $\sigma_i \geq \sigma_m + b(\sigma_M - \sigma_m)$. σ_m and σ_M are the smallest and largest size possible for the specified polydispersity δ (see Table 1).

tural complexity and nontrivial mechanical response. The potentials of effective interaction that we developed are able to include a few features obtained from experiments and molecular scale simulations of calcium silicate hydrates (e.g., the polydispersity and the strain at rupture). We have showed here that accounting for the interfacial zone at the “contact” points between the nanoparticles is key to obtain elastic constants of the model gels that agree well with the results from nanoindentation experiments. This led to a significant improvement of the computed elastic constants, compared to a previous version of our model¹⁵.

We use a Monte Carlo space-filling algorithm to generate the model colloidal structures, followed by relaxation to zero stress. The algorithm is based on random insertion of polydisperse particles into a simulation box, and on minimization of the total interaction energy. This protocol has the advantage of producing systems with high packing fractions, in the range of those measured experimentally by nanoindentation on the C–S–H gel. We find that the resulting distributions of particle sizes (and hence structural heterogeneities) inside the simulation box are of geometric type, a characteristics that is consistent with the results of small angle neutron scattering experiments^{17,43}.

The response of our model structures to shear deformation is elastic only at small applied strain. Some marked nonlinearities appear at greater strain levels, and eventually the systems undergo yielding. After yielding, the shear stress oscillates around a maximum constant value that is a measure of the shear strength of our model C–S–H gels. We have found that the shear strength increases very significantly with the polydispersity. This is consistent with the fact the higher polydispersity allows for denser packing. We have also found that the range of strain in which the response of the system is elastic, i.e. reversible upon unloading, increases with the polydispersity. This implies that the strength of our model gels increases

faster than the elastic constants, upon increasing the polydispersity, viz. the packing density. A similar trend is also shown by nanoindentation measurements on real C–S–H gel¹⁰.

Structural heterogeneities are certainly important for the mechanics of these complex, soft matter systems, for example with regard to strain localization and triggering of non-linear responses. Despite critical for the performance of the material, these issues remain mainly unexplored. We have investigated the accumulation of irreversible processes in the mechanical response, by relaxing our configurations from different levels of applied strain, back to zero shear stress. The results show that once yielding is triggered, the accumulation of irreversible strain is similar for all the model systems irrespective of their polydispersity. Nevertheless, the amount of irreversibility quantified by the decrease of total interaction energy during the shear tests is remarkably smaller in the highly polydisperse systems. We have shown that the mechanisms of accumulation of irreversible deformations (“plastic rearrangements”) are discrete events, whose signature is an abrupt drop of shear stresses and pressure, accompanied by large non-affine displacements of the particles. By monitoring the non-affine displacements of subsets of particles within certain ranges of sizes, we have shown that small particles undergo larger non-affine displacement during a plastic event, i.e. they play a primary role in the accumulation of irreversible deformations. By contrast, large particles behave as inclusions that hardly move and that need to be “excluded” by the motion of the rest of the system in order for yielding to occur. This may be the reason why highly polydisperse systems display a broad initial elastic regime: it is hard to circumvent large particles and exclude them from the plastic flow.

In conclusion, our colloidal description of C–S–H gels has allowed gaining significant new insight into the role of nano-scale structural heterogeneities and in particular polydispersity. This opens new, unexplored ways to optimize the mechanical performance of the C–S–H gels, provided we also improve our knowledge on how the complex chemistry of the cement pastes affects the formation process of these gels, the size of the colloidal units, and the interactions between them. A deeper understanding of the issues addressed here and suggested by our soft-matter physics approach can be the key to the development of innovative and more sustainable cements.

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