

# Water-Dependent Micromechanical and Rheological Properties of Silica Colloidal Crystals Studied by Nanoindentation

Francisco Gallego-Gómez<sup>1</sup>, Víctor Morales-Flórez<sup>2</sup>, Álvaro Blanco<sup>1</sup>, Nicolás de la Rosa-Fox<sup>3</sup> and Cefe López<sup>1</sup>

<sup>1</sup>Instituto de Ciencia de Materiales de Madrid, ICMM (CSIC), Madrid, Spain

<sup>2</sup>Instituto de Ciencia de Materiales de Sevilla, ICMS (CSIC-Univ. Sevilla), Sevilla, Spain

<sup>3</sup>Departamento de Física de la Materia Condensada, Univ. Cádiz, Cadiz, Spain

francisco.gallego@icmm.csic.es

Solid colloidal crystals (CCs) have many applications in *e.g.* photonics, energy conversion, sensing and as templates, for which diverse mechanical requirements are mandatory, so that the study of issues like the stability against deformation is essential. They are also used for modeling of atomic systems, where mechanical features may impart relevant information. However, mechanical testing of CCs is not well-established and very little is known about their mechanical properties and governing factors.

We show the suitability of nanoindentation to study in detail the micromechanical response of CCs made of bare (without extrinsic ligands) submicrometer silica spheres [1]. The sensitivity to displacements smaller than the spheres size, even resolving discrete events and superficial features, revealed particulate features with analogies to atomic crystals (Figure 1). Significant robustness, long-range structural deformation and large energy dissipation were found. In silica CCs, the hydrophilic character of the particles leads to the presence of abundant physisorbed water (about 8 wt. %), and capillarity becomes relevant as water forms liquid bridges, which anticipates a link to wet granular matter. Experiments on heated opals (up to 150 °C), in which the water content was easily controlled, elucidated the influence of capillary cohesion on the mechanical strength (Figure 2). Rate-dependent

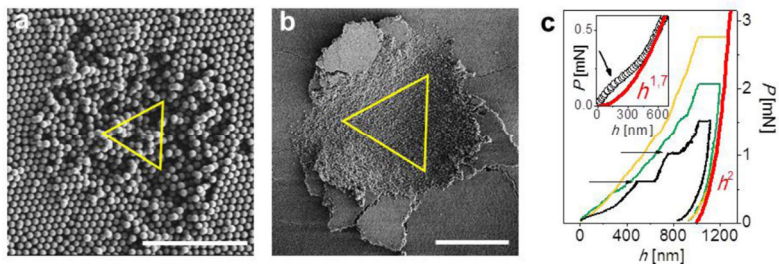
nanoindentation revealed that the adsorbed water endowed silica CCs with properties of wet granular materials like viscoplasticity (Figure 3). A novel ‘non-granular’ CC was fabricated by substituting capillary bridges with silica necks to directly test non-water-dependent mechanical response. Silica CCs, as specific (nanometric, ordered) wet granular assemblies with well-defined configuration, may be useful model systems for granular science and capillary cohesion at the nanoscale.

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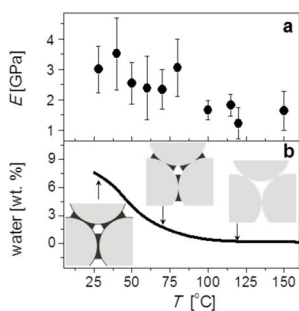
## References

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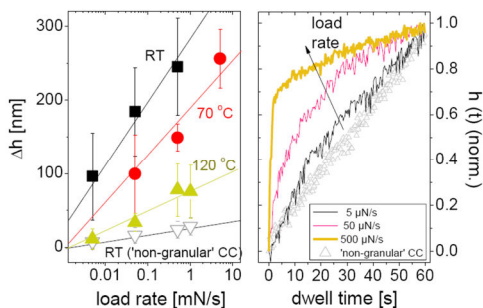
- [1] F. Gallego-Gómez, V. Morales-Flórez, Á. Blanco, N. de la Rosa-Fox, C. López, *Nano Letters*, 12 (2012) 4920–4924.



**Figure 1:** (a, b) SEM micrographs of residual indents at  $h_{max} = 500$  and  $4600$  nm (scale bars are  $5$  and  $20$   $\mu\text{m}$ ), respectively. Yellow triangles delimit the intersection areas of the Berkovich indenter (at maximum penetration  $h_{max}$ ) with the surface plane. (c) Typical load-depth curves with  $h_{max} = 1000$  nm performed at different load rates ( $5$ ,  $50$  and  $500$   $\mu\text{N/s}$  –black, green and orange lines, respectively). Two pop-in events, designated by arrows, are visible at the lowest rate. Inset: zoom-in of the loading curve at early penetration stage (rate of  $50$   $\mu\text{N/s}$ ); the arrow indicates a characteristic initial displacement burst. Red curves are fitting power-law functions.



**Figure 2:** Temperature-dependence of the Young modulus  $E$  (a) measured at  $h_{max} = 600$  nm, and content of adsorbed water in the CC (b). Sketches in (b) depict the distribution of water (black) between the opal spheres (gray) at  $T = 28$ ,  $70$  and  $120$   $^{\circ}\text{C}$  (proportions are maintained).



**Figure 3:** (a) Creep displacement  $\Delta h$  after dwell time of  $60$  s as function of the load rate (symbols) and linear fits (lines), measured in CCs at RT,  $70$  and  $120$   $^{\circ}\text{C}$ , and in the modified, 'non-granular' CC (at RT). (b) Normalized transient creep  $h$  ( $t$ ) measured at RT in CCs at  $5$ ,  $50$  and  $500$   $\mu\text{N/s}$  and in the modified CC (at  $50$   $\mu\text{N/s}$ ). All experiments were performed at constant load  $P = 1.5$  mN.