

## Crystallization Mechanism of Hard Sphere Glasses

Eduardo Sanz,<sup>1,\*</sup> Chantal Valeriani,<sup>1</sup> Emanuela Zaccarelli,<sup>2</sup> W. C. K. Poon,<sup>1</sup> P. N. Pusey,<sup>1</sup> and M. E. Cates<sup>1</sup>

<sup>1</sup>*SUPA, School of Physics and Astronomy, University of Edinburgh,  
Mayfield Road, Edinburgh, EH9 3JZ, Scotland*

<sup>2</sup>*CNR-ISC and Dipartimento di Fisica, Università di Roma “La Sapienza”, P.le A. Moro 2, I-00185 Roma, Italy*

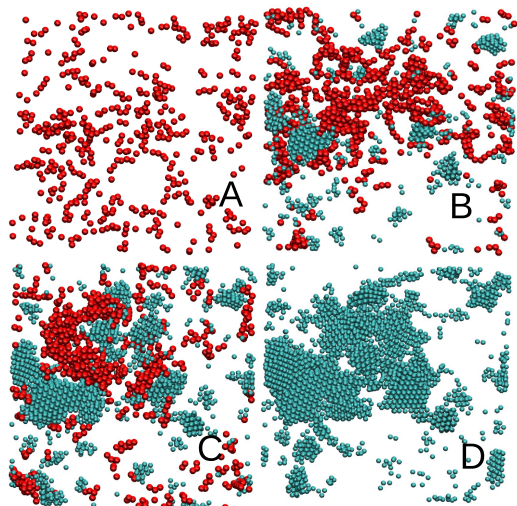


FIG. 1. Slab in the  $xy$  plane showing the 5% most mobile particles (in red) and the crystalline particles (in light blue) at time  $t = 0$  (A),  $t = 320$  (B),  $t = 640$  (C) and  $t = 1280$  (D). Mobile particles are ranked by the distance they move between the time of the frame at which they are shown and the subsequent frame. They are spatially correlated with crystalline ones and have a higher tendency to become crystalline than “average” amorphous particles.

In supercooled liquids, vitrification generally suppresses crystallization [1]. Yet some glasses can still crystallize despite the arrest of diffusive motion [2]. This ill-understood process may limit the stability of glasses, but its microscopic mechanism has not been probed yet. Here we present extensive computer simulations addressing the crystallization of monodisperse hard-sphere glasses at constant volume (as in a colloid experiment). Multiple crystalline patches appear without particles having to diffuse more than one diameter. As these patches grow, the mobility in neighbouring areas is enhanced, creating dynamic heterogeneity with positive feedback. The future crystallization pattern cannot be predicted from the particle coordinates alone: crystallization proceeds by a sequence of stochastic micro-nucleation events, correlated in space by emergent dynamic heterogeneity.

Figure 2 shows the evolution of an initial state with periodic density pattern, following two different tra-

jectories (white arrows) from identical initial particle coordinates, but with different initial velocity choices (drawn at random from the thermal distribution). The black arrow shows a run where velocities are randomized after  $X$  reaches 0.05. The subsequent evolution is again altered, even though significant crystallinity was already present. At no stage do we find the future evolution to depend reproducibly on coordinates alone, although crystallites are more likely to form in regions of high  $Q_6$  than elsewhere. The crystallization mechanism thus comprises a sequence of stochastic ‘micro-nucleation’ events.

\* Corresponding author: [esanz@ph.ed.ac.uk](mailto:esanz@ph.ed.ac.uk)

- [1] P. G. Debenedetti and F. H. Stillinger, *Nature* **410**, 259 (2001).  
[2] E. Zaccarelli and C. Valeriani and E. Sanz and W. C. K. Poon and M. E. Cates and P. N. Pusey, *Phys. Rev. Lett.* **103**, 135704 (2009).

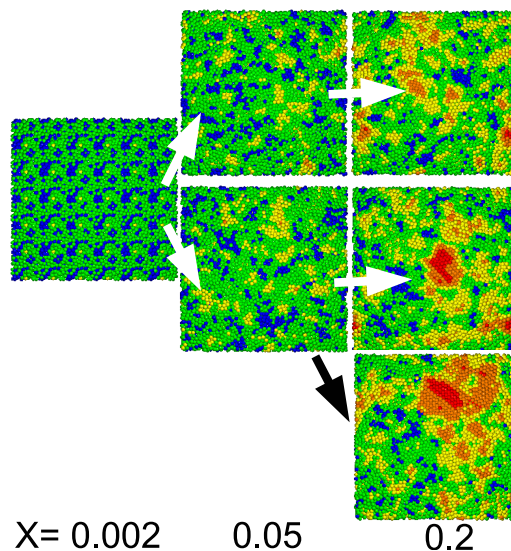


FIG. 2. Slab of the system for various values of the evolving crystallinity  $X$ . Particles are coloured according to the degree of crystalline order in their neighbourhood (blue,  $0 < Q_6 < 0.15$ ; green  $0.15 < Q_6 < 0.25$ ; yellow  $0.25 < Q_6 < 0.35$ ; orange  $0.35 < Q_6 < 0.45$ ; red  $0.45 < Q_6 < 0.55$ ). The initial state (left) has a periodic density pattern that is quickly forgotten.