Crystallization versus vitrification in hard spheres

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A collective of hard spheres is, arguably, the simplest non-trivial system that displays a fluid-solid transition. This was discovered in pioneer computer simulations by Alder and Wainwright in the late 50s[1] and observed experimentally in suspensions of hard-sphere-like colloids by Pusey and van Megen about 30 years later[2]. Besides the solid and the fluid phases, Pusey and van Megen observed glassy samples, some of which were able to become crystalline after some time. This motivated our studies during the past few years on the relation between the glass transition and crystallization in hard-sphere systems.

We started by establishing the location of the dynamical glass transition in size monodisperse hard-sphere systems. Since crystallization in this system readily occurs before the dynamics shows any signature of arrest there has been some debate on whether or not there is a true glass transition for this system. By comparing the dynamics of monodisperse and polydisperse systems we concluded that there is indeed a glass transition and that crystallization occurs with no diffusion for densities larger than that corresponding to the dynamic transition[3,4].

More recently, we have focused our efforts in understanding and characterizing the regime in which crystals appear and grow with no particle diffusion[5]. We observed that particles are able to rearrange gradually into a crystalline environment by rattling motion alone, following a crystallization pathway that is nonetheless chaotic and unpredictable from the configuration. The chaotic and gradual nature of the mechanism is illustrated in the figure. This mechanism is self-sustained because the emergence of crystals increases the mobility of neighboring particles by free volume release. We have also analyzed the structural properties of the crystalline clusters growing via this mechanism, concluding that beyond the density at which crystallization times are shorter than diffusion times the structural properties of the growing clusters do not change with density[6].

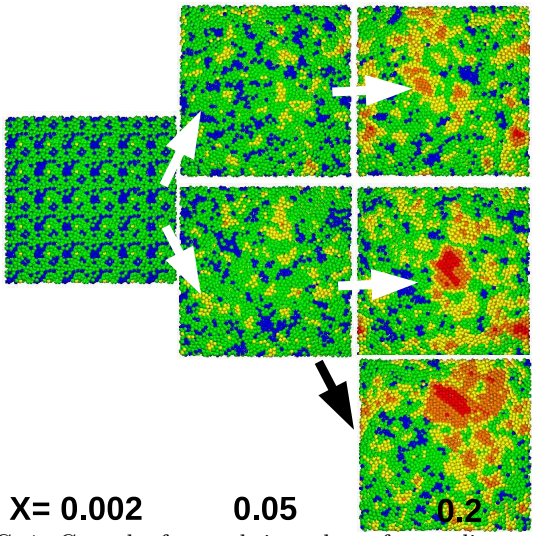

FIG. 1. Growth of crystals in a glass of monodisperse hard spheres at volume fraction 0.61.

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