Physicists find missing link between glass formation and crystallization

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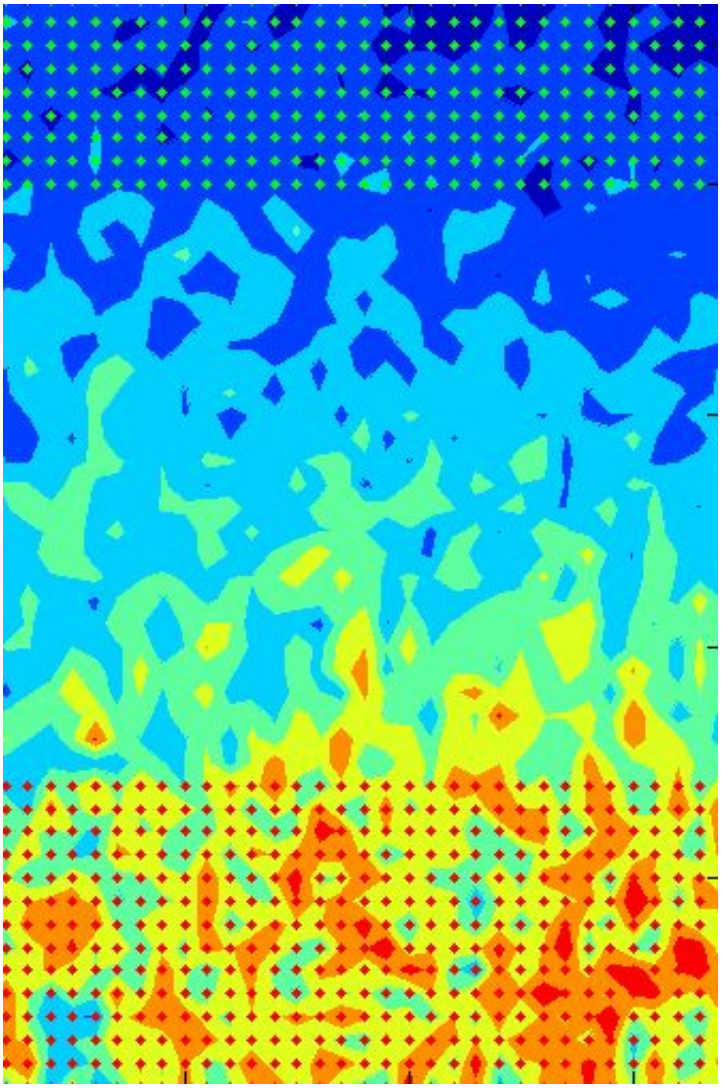

Solidification under sedimentation: The dynamic map illustrates the speed of the particles in the model system. Regions with low speeds are marked in red and orange while those with higher speeds are blue. Red dots show where a solid has already formed. Similar maps were taken during glass formation, but due to the

overall homogeneity of the process they look somewhat more boring. Credit: KOMET336, Institute of Physics, JGU

Glasses are neither fluids nor crystals. They are amorphous solids and one of the big puzzles in condensed matter physics. For decades, the question of how glass forms has been a matter of controversy. Is it because some regions freeze their thermal motion? Or is it because there are particles or clusters which do not fit to form a crystal? At least for the model system of hard spheres, researchers at Johannes Gutenberg University Mainz (JGU) in Germany have now taken a major leap in reconciling these two opposing views.

Using a clever combination of light scattering and microscopy, they were able to demonstrate that within a melt of hard spheres small compacted regions form comprising a few hundred spheres. These so-called precursors are the starting point for both crystallization at moderate undercooling and glass formation at large undercooling. The researchers observed that the motility of particles within these precursors was extremely limited and decreased further with undercooling, while their number rapidly increased. With only few precursors present, crystallization may still start at the surface. However, the more of these precursors are present, the more of their surface they block. Moreover, with the precursor number still increasing in time, the system soon gets jammed and all further dynamics cease. This means that from a certain point in undercooling and time onwards, crystal formation is no longer possible.

The results of this research work performed in the JGU Graduate School of Excellence "Materials Science in Mainz" (MAINZ) have recently been published in the journal *Nature Physics* as an advanced online publication.

Glass and crystal are two different structures but either of these can form from a melt. In the case of glass, the atoms retain their disorganized state, similar to that seen in liquids, while in crystals they assume a very regular lattice structure. It is the solidification process that determines which type of structure will be formed. The physics experiments carried out at Mainz University did not focus on the fabrication of a particular glass, such as for use in safety windows or fiber optics for communication purposes. They were rather aimed at an advanced understanding of the glass formation process in general, which is a traditional research topic in the JGU Condensed Matter Physics group. The researchers were looking at the formation of amorphous solids in general, and they used an experimental model system for hard spheres. Here the undercooling is not realized by decreasing the temperature, but by increasing the concentration of polymer spheres. Crystals form when more than 50 percent of the volume is taken by the hard spheres in the suspension, while glasses form at more than 60 percent. Such systems of micro-sized polymer spheres in a solvent have been subject to intense research over the last decades, because they closely mimic the behavior of ideal hard spheres which are well studied by theory and computer simulation.

It has been known since the 1990s that hard-sphere melts contain both regions of differing density and order as well as regions that vary in terms of the motility of the atoms, i.e., regions of structural and dynamic inhomogeneity. Since then, the role played by these two factors during the process of solidification has been the subject of intense debate by theoretical physicists. "What we have now ascertained is that these regions are in fact identical, thus laying the controversy to rest," said Professor Thomas Palberg of the Institute of Physics at Mainz University, explaining the results of his research.

Mapping motility within hard-sphere suspensions

In order to understand the processes taking place, Sebastian Golde, a member of the MAINZ Graduate School of Excellence and Palberg's research team, investigated hard-sphere model systems in an optical experiment. "We were able to show that the regions with more densely packed spheres and a little more order coincide with those areas where the hard spheres clearly move more slowly," stated Golde. This means that the long-standing enigma concerning the two different regions of inhomogeneity has been resolved.

The method used is a combination of static and dynamic light scattering. "We analyze how much light of a laser beam directed at the sample is scattered in a given direction. This tells us the sample structure. But we also analyze how it flickers after scattering. This tells us how fast the particles move," said Golde, who himself built his instrument designed by Dr. Hans Joachim Schöpe, who recently moved to the University of Tübingen. Moreover, utilizing a clever imaging system, Golde was able to obtain so-called dynamic maps with unprecedented resolution somewhat smaller than the precursors. Like an image produced by a camera, the result is a kind of photo that captures the activity of the dynamics within the various regions. Thus, the researchers observed that as time proceeded, ever more small dense areas with slow-moving spheres were generated. Their formation speed decides whether there is enough time left for the formation of crystals before jamming occurrs. Since the precursor formation speed is related to the hard-sphere concentration, one finds crystallization at low concentrations of hard spheres. On the other hand, at higher concentrations these compacted regions become quickly arrested and the system solidifies into a glass.

"In other words, glass results when so many crystallization precursors are formed that they in effect arrest each other," clarified Palberg. "For us, this means that an unexpected and fascinating link has been found between the two solidification scenarios. Arguably, this was one of the most important missing pieces of the puzzle." The findings are believed

to be very general, but the investigation should clearly be extended also to other model systems to further support the view of coinciding structural and dynamical inhomogeneities being responsible for glass formation.

More information: Sebastian Golde et al. Correlation between dynamical and structural heterogeneities in colloidal hard-sphere suspensions, *Nature Physics* (2016). DOI: 10.1038/NPHYS3709

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