Colloids reinforce glass theory

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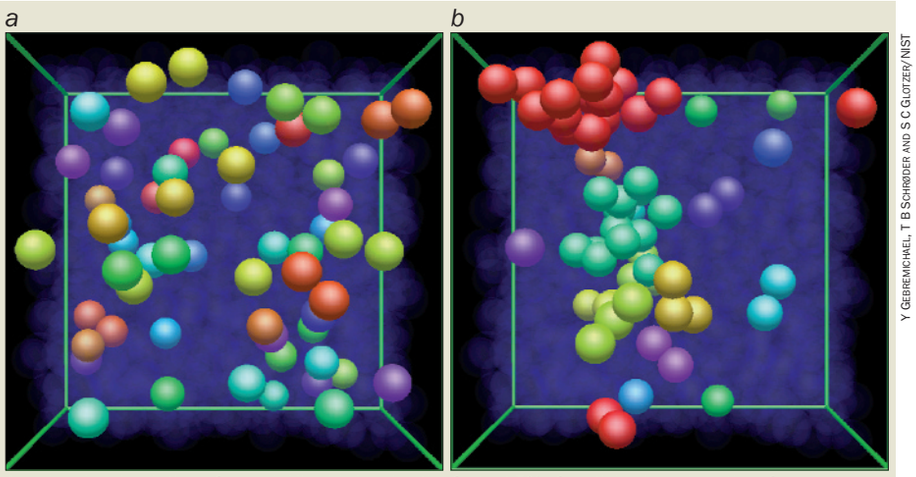

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A molecular simulation of a model liquid showing the fastest 5% of particles in a given time frame when the liquid is (*a*) far from the glass transition and (*b*) closer to the glass transition. In both cases, fast particles that are immediately next to each other, and are thus contained within the same "cluster", are shown by the same colour. Weeks and collaborators confirmed the clustering of fast particles in their pioneering confocal-microscopy experiments on dense colloidal suspensions.

In 1995 Philip Anderson wrote that the glass transition remains the deepest and most important unsolved problem in solid-state physics. Why is there so much mystery surrounding the seemingly simple solidification of a liquid into a disordered solid, like glass – one of the most ubiquitous forms of matter?

Part of the mystery lies in the dramatic slowing down of molecular motion that accompanies glass formation. Molecules in the liquid can move 10^{13} times faster than those in the disordered solid. Yet the molecular structure of the liquid is hardly distinguishable from that of the glass. Contrast this with the very different structure of an ordered solid, or crystal, in which the molecules are arranged in periodic arrays.

Liquids form glasses when they become very dense, and/or very cold. When this happens, the molecules become crowded, or "jammed", and cannot move unless their neighbours also move. This behaviour is similar to the crowded, concerted motion of people at a train station during rush hour. It is this increasing need for co-operativity in molecular motion that is thought to lie at the heart of the glass transition (see "Glass physics: still not transparent" by K Binder *et al. Physics World* December 1999 p54). Unfortunately, experimental techniques are not yet able to directly probe the motion of an individual molecule relative to a particular neighbour, or to directly observe the co-operative rearrangement of groups of molecules.

Until very recently, computer simulations of so-called model liquids were the only method capable of probing molecular motion at this level of detail. In a model liquid, the individual atoms or molecules interact via specified forces and move according to Newton's second law of motion. Over the past few years, such simulations have provided many intriguing predictions concerning the co-operative nature of molecular motion in glass-forming liquids. One of the most striking is that a population of fast molecules emerges amidst the increasingly sluggish motion in the liquid. These fast molecules move co-operatively in string-like paths, and cluster into transient, fractal structures that grow rapidly in size as the glass transition is approached.

The predictions have now been confirmed by Eric Weeks and co-workers at Harvard

University, the University of Pennsylvania and Edinburgh University. The research team made the breakthrough studying suspensions of colloids that form glasses when they become very dense (E Weeks *et al.* 2000 *Science* **287** 627).

Colloids are large particles, typically between several nanometres and a few microns in size, and are found in paints, inks, cosmetics and other everyday products. Scientists also think of them as model liquids because they obey the laws of statistical mechanics (see *Physics World* May 1997 p27). Colloids that act essentially as hard spheres and interact only when they touch are perhaps the simplest example of a glass-forming system. Because of their large size, which is roughly the wavelength of visible light, colloids can be seen through an optical microscope.

Weeks and co-workers used a confocal microscope – which can focus to different depths in the suspension – a video camera and image-analysis software to record the positions of individual colloidal particles in 3-D over many hours. In this way, the researchers found that roughly 5% of the particles moved together in groups or "clusters" at any given time, while the rest of the liquid remained relatively static. As predicted by simulations of several model glass-formers, a wide range of cluster sizes was observed, and the typical cluster size grew rapidly as the glass transition was approached (see figure).

Willem Kegel and Alfons van Blaaderen of the University of Utrecht in the Netherlands have also observed correlated particle motion as well as regions of high and low mobility in similar experiments with colloidal suspensions (*Science* 2000 **287** 290–293). However, their experiments were restricted to observing motion within 2-D slices of the sample.

Both studies demonstrate the increasing significance of co-operativity in enabling particle motion as the colloids become denser. Like in the train-station analogy, as the particles become crowded, their motion becomes increasingly difficult. An increasing number of particles must move together in order to move at all.

The pioneering work of Weeks and co-workers establishes confocal optical microscopy as a powerful tool with which to probe the dynamics of fluids composed of large numbers of micron-sized particles. The researchers are quick to acknowledge the role of simulation in inspiring and guiding their experiments. Indeed, computer simulations played a unique role in identifying the most relevant quantities to be measured. They have also lead to a statistical-mechanical framework within which to describe correlated particle motion.

The partnership between experiments and simulations is ideally suited to addressing the outstanding questions central to the glass transition. How does co-operative motion arise in the first place? How is the particle motion related to the underlying liquid structure? And how is co-operativity related to the overall slowing down of relaxation in the liquid?

Glass-transition phenomena and the co-operative motion of molecules are important for a wide range of systems beyond window glass. Breakthroughs in our understanding of the glass transition are likely to have an impact on problems ranging from the vitrification of pharmaceuticals to nanotribology and the anomalous diffusion of molecules in plastics. Furthermore, understanding motion in "jammed" systems may have profound effects on other fields, such as protein folding, the flow of granular materials, the shearing of wet foams and the deformation of bulk amorphous metals.

As new experimental techniques are developed, it may one day be possible to directly observe co-operative motions of atoms and molecules. In the meantime, optical-microscopy experiments on model colloidal fluids, combined with simulations of atomic, molecular and polymeric liquids, will continue to shed light on the universal features of glass formation.