AMORPHOUS SOLIDS

Glasses pinned down

Laser tweezers can be used to control particles in a colloidal glass, thereby influencing the dynamics of their neighbours. The range of this influence — and how it changes — may provide a structural mechanism to explain the solidity of glasses.

Eric R. Weeks

Glassy materials are amorphous solids: they have a liquid-like structure, but do not flow. Lower their temperature towards the glass transition and you'll see the viscosity rise smoothly and dramatically by ten or more orders of magnitude. There is no discontinuous change in the flow properties at a specific temperature — as is seen with crystallization — and no discontinuous change in the structure either[1]. This makes explanations for the solidity of crystalline materials difficult to apply to glasses. But now, writing in *Nature Physics*, K. Hima Nagamanasa and co-workers[2] report experiments with colloidal samples that reveal subtle structural effects near the glass transition — suggesting potential structural mechanisms to explain the solidity of glasses.

In 2004, the idea of 'point-to-set' correlations was proposed[3] and later confirmed by simulations[4]. The idea was to take a simulation of a liquid, 'pin' all particles outside a spherical cavity of radius R (Fig. 1a) and then continue to simulate the behaviour of the particles within the cavity. For large enough R, the behaviour in the centre of the cavity was independent of the frozen boundary. However, for R less than some critical value, R_C, the sample within the cavity could no longer completely rearrange. R_C increased as T approached the glass transition temperature, identifying a growing length scale for subtle structural order.

The terminology point-to-set comes from correlating the dynamics observed at the point at the centre of the cavity, and the set of frozen particles at the cavity surface a distance R away[5]. The key idea for studying point-to-set correlations is that the frozen boundary is taken from the same initial equilibrium configuration as that of the particles within the cavity. These are 'amorphous boundary conditions', but in this case, the amorphous structure isn't arbitrary — rather, it is consistent with the sample within the cavity. This detail is important, as flat boundaries are well known to introduce local ordering[6].

Nagamanasa *et al.*[2] directly tested point-to-set correlations using laser tweezers to precisely control the positions of colloids — their model system of choice. Instead of temperature, the key control parameter for colloids is particle concentration. At a sufficiently high particle concentration, a colloidal sample undergoes a transition with a remarkable number of similarities to thermal glass transitions[7].

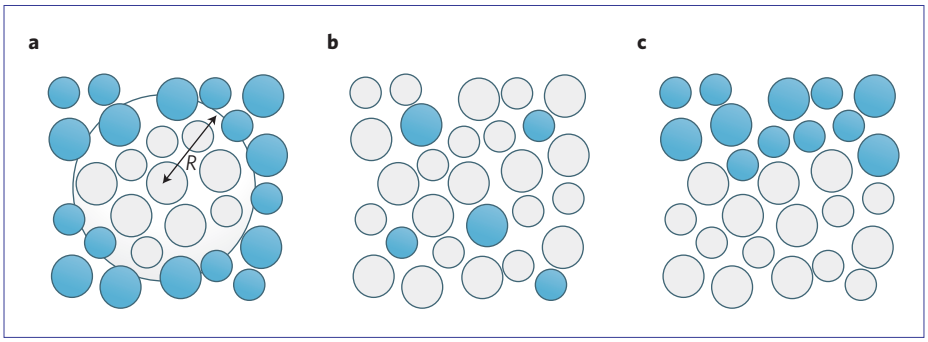


Figure 1 | Sketches of different geometries for testing point-to-set correlations. **a**–**c**, In each illustration the shaded particles are 'pinned' — they are not allowed to move. In **a**, R is the radius of a spherical cavity containing un-pinned particles.

In their experiments, Nagamanasa *et al.*[2] used a quasi-two-dimensional colloidal sample as their glass-forming system. The heavy particles sank to the bottom of their sample chamber to form a monolayer. The sample was composed of two different particle sizes, designed to frustrate ordering. Once the sample was formed, the authors used holographic laser tweezers capable of trapping dozens of particles simultaneously to replicate the simulation methods, holding a subset of the particles in desired positions. This control allowed them to manipulate the colloidal particles in ways that would be impossible for molecular glasses. This enabled direct comparison to the simulations, and thus the first experimental study of point-to-set correlations.

In a previous paper[8], the group used their laser tweezers to pin randomly chosen particles at several different pinning concentrations (Fig. 1b). In this experiment, as the pinning concentration was increased up to 12% the timescale for rearrangement of the unpinned particles grew by a factor of four to five. In the second paper[2], the group used their laser tweezers to grab a stripe of particles to form a wall in the sample, as shown in Fig. 1c — a geometry proposed and simulated recently[9]. They observed that near the wall particles rearranged slowly — or not at all. The mobility gradually recovered to match bulk conditions farther from the wall, with an exponential recovery. The exponential decay length was thus the point-to-set length for the experiment, and it was found to grow by a factor of four as the glass transition concentration was approached.

The concept of point-to-set correlations was originally motivated by random first-order transition (RFOT) theory[10,11], which holds that there is a vast variety of locally favourable aperiodic structures, and that the sample is tiled with a 'mosaic' of these structures[11], with a surface tension at the interfaces between them. Rearrangements within such a material (in the liquid state near the glass transition) depend on the details of the sizes and shapes of these structures, and the effective surface tension acting between them. If the length scale of such structures grows near the glass transition, and rearrangements become more difficult, then this could explain why the viscosity of a liquid increases dramatically as the temperature is lowered towards the glass transition temperature. This is precisely the story suggested by the colloidal experiments[2]. In fact,

© 2015 Macmillan Publishers Limited. All rights reserved

Nagamanasa *et al.* showed that details of their experiment matched other predictions of RFOT. For example, particles with large displacements occur in localized groups, and the shape of these groups becomes more compact as the glass transition is approached.

Ideas of a subtle structural length scale in amorphous materials are more general than the RFOT theory[1,12]. Nonetheless, the experimental work of Nagamanasa *et al.*[2] confirms the existence of the point-to-set length scale, and thus provides important experimental evidence supporting the RFOT ideas. Ultimately, the combination of the simulations and experiments reveals crucial relations between amorphous structure and dynamics — suggesting that amorphous structure may not be quite as amorphous as we thought. ❐

Eric R. Weeks is in the Department of Physics at Emory University, Atlanta, Georgia 30322-2430, USA.
e-mail: erweeks@emory.edu

References

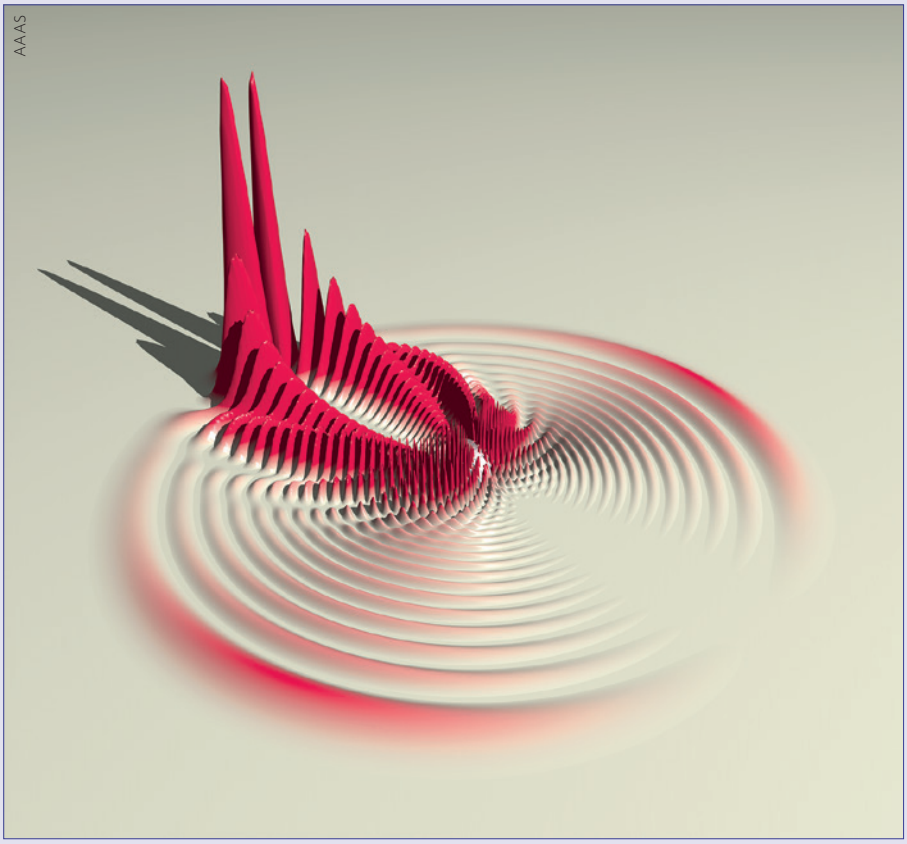
1. Royall, C. P. & Williams, S. R. *Phys. Rep.* **560,** 1–75 (2015).
2. Nagamanasa, K. H., Gokhale, S., Sood, A. K. & Ganapathy, R. *Nature Phys.* **11,** 403–408 (2015).
3. Bouchaud, J-P. & Biroli, G. *J. Chem. Phys.* **121,** 7347–7354 (2004).
4. Cavagna, A., Grigera, T. S. & Verrocchio, P. *Phys. Rev. Lett.* **98,** 187801 (2007).
5. Montanari, A. & Semerjian, G. *J. Stat. Phys.* **125,** 23–54 (2006).
6. Desmond, K. W. & Weeks, E. R. *Phys. Rev. E* **80,** 051305 (2009).
7. Hunter, G. L. & Weeks, E. R. *Rep. Prog. Phys.* **75,** 066501 (2012).
8. Gokhale, S., Nagamanasa, K. H., Ganapathy, R. & Sood, A. K. *Nature Commun.* **5,** 4685 (2014).
9. Berthier, L. & Kob, W. *Phys. Rev. E* **85,** 011102 (2012).
10. Lubchenko, V. & Wolynes, P. G. *Ann. Rev. Phys. Chem.* **58,** 235–266 (2007).
11. Kirkpatrick, T. R., Thirumalai, D. & Wolynes, P. G. *Phys. Rev. A* **40,** 1045–1054 (1989).
12. Watanabe, K., Kawasaki, T. & Tanaka, H. *Nature Mater.* **10,** 512–520 (2011).

Published online: 13 April 2015

MOLECULAR PHYSICS

Tiny giant

Behold this little beast: a trilobite Rydberg dimer (pictured). These exotic trilobite molecules — named for the resemblance between their electron probability distributions and fossilized ancient marine creatures — are unusual in many ways. Theoretically predicted by Chris Greene and co-workers more than a decade ago (*Phys. Rev. Lett.* **85,** 2458–2461; 2000), they are ultra-long-range molecular Rydberg states. These are highly excited states with very large principal quantum numbers and high orbital angular momenta coupled to a ground-state atom of the same species. Due to the strong localization of the electron clouds, these dimers are expected to possess huge permanent electric dipole moments, of the order of thousands of debye. And this is quite surprising given that homonuclear molecules are symmetric and therefore should not have a dipole moment in the first place.



Greene *et al.* predicted that trilobite Rydberg molecules could be produced in Bose–Einstein condensates, and the obvious experimental target has been rubidium. But Donald Booth and colleagues have now shown that caesium atoms, due to peculiarities in their low orbital angular momentum energy states, can be bound in a hybrid molecule with a mixture of high and low orbital angular momentum states, yielding permanent electric dipole moments of thousands of debye (*Science* **348,** 99–102; 2015). To put this into perspective, the dipole moment of water is 1.85 debye and even very polar molecules like sodium chloride have dipole moments of 9 debye.

The caesium dimer observed by Booth *et al.* has a bond length of around 100 nanometres. This is huge — stretching the very definition of a chemical bond. In comparison, the diameter of a C_{60} fullerene is about 1 nanometre, with its carbon bonds measuring roughly 1 ångström. Still, this may not come as such a surprise if we recall that the orbits of Rydberg electrons can be as large as 8 micrometres: comparable — or even larger — than the Bose–Einstein condensate they are part of.

One can readily envisage applications for these trilobite Rydberg dimers, ranging from ultracold chemistry to the study of strongly correlated many-body physics. But irrespective of whether these will materialize or not, creating these molecules adds a new creature to the ultracold atom menagerie of exotic states.

IULIA GEORGESCU

© 2015 Macmillan Publishers Limited. All rights reserved