

## STRUCTURAL GLASSES

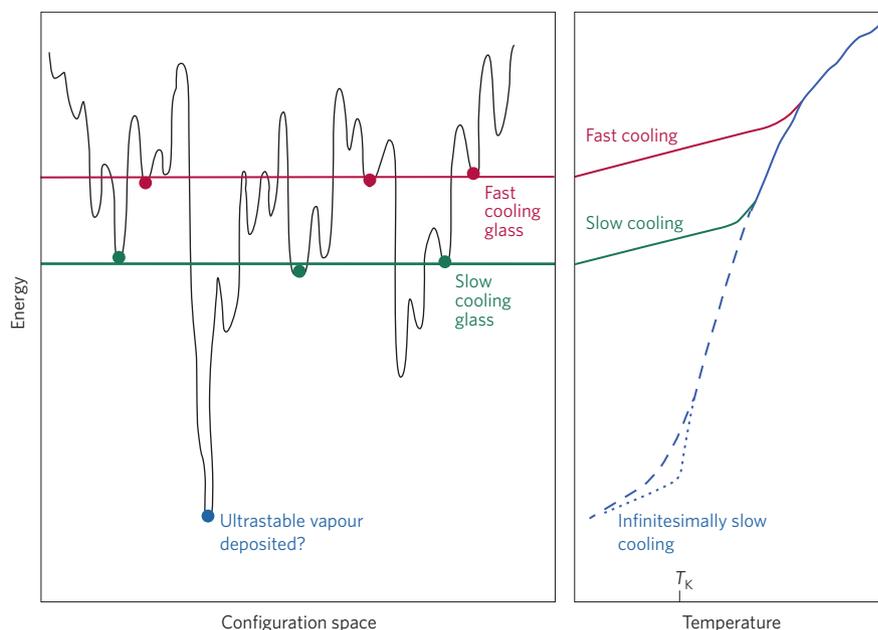
## Flying to the bottom

It has been shown that glasses prepared by physical vapour deposition have extraordinary stability. A computer algorithm that mimics such a process has now identified the optimal deposition temperature and the glasses' structural features.

Giorgio Parisi and Francesco Sciortino

Glasses retain in their structure information about their history and the way they were initially prepared. To understand this, it is useful to think of glasses in the context of a potential energy landscape — a complex corrugated multidimensional surface composed of basins of different depths and widths<sup>1,2</sup> (Fig. 1, left). In this energy landscape, a liquid at equilibrium is continuously exploring different regions, whereas a glass is trapped in a specific basin, the height of which is related to the glass's properties. The lowest basin for a disordered state would thus correspond to a glass that has the strongest cohesive energy and optimal thermal stability. When cooling a liquid to form a glass (that is, at conditions at which the nucleation of the thermodynamically stable crystal phase is bypassed), the faster the cooling rate is, the higher up in the energy landscape the glass is trapped and the more similar its structure is to that of a high-temperature liquid. So far, glasses cooled at the slowest experimentally accessible cooling rate have however remained trapped in basins significantly higher than those that are supposed to lie deepest in the energy landscape.

Glasses have also been prepared by destabilization of the crystal structure, or by physical vapour deposition of atoms or molecules on a cold substrate. But as with the fast-cooled glasses, these methods also resulted in trapped configurations that are high in the energy landscape. In fact, by progressively depositing particles on a substrate the generation of a disordered structure reminiscent of that of high-temperature liquids would be expected. This is why the recent discovery that exceptionally stable organic glasses can be produced by vapour deposition when the deposition rate is low and the deposition temperature is high (significantly higher than in previous studies) came as a big surprise<sup>3</sup>. Neutron refractivity experiments on these ultrastable glasses showed that molecules lying at the top of the deposited film had enhanced mobility<sup>3</sup>, which is



**Figure 1** | The energy landscape of a glass. Schematic of a one-dimensional projection of a potential energy landscape that is rugged (that is, with multiple basins and barriers between them; left) and temperature dependence of the energy of a glass (right). In equilibrium, a liquid explores basins with a characteristic energy depth. Such a depth decreases with decreasing temperature. When a liquid is cooled, it goes out of equilibrium at a temperature that depends on the cooling rate. The liquid thus remains trapped in the basins that are commonly explored at that temperature; the slower the cooling, the lower the energy of the basin where the system will remain trapped. Results from Singh and colleagues<sup>5</sup> and from ref. 3 suggest that physical vapour deposition can result in an effective method for generating glass states that are trapped in the lowest basins of the landscape. The blue curve indicates the equilibrium value of the energy (solid line) and expected extrapolations (dashed lines) for two ideal cases in which the cooling rate is infinitesimally slow (the dashed line with a kink would imply the existence of a truly thermodynamic transition at  $T_K$ , the finite temperature at which the deepest basins of the landscape are explored; see main text for details). Understanding which of the two possible extrapolations is correct remains an unsolved problem in glass physics.

suggestive of the existence of a mobile (liquid) surface layer constantly regenerated by the incoming flux of molecules (once deposited, a layer of molecules becomes glassy in a few seconds). Apparently, in the same way the surfaces of crystals are not always so crystal-like, the surfaces of glasses may not be so glassy<sup>4</sup>.

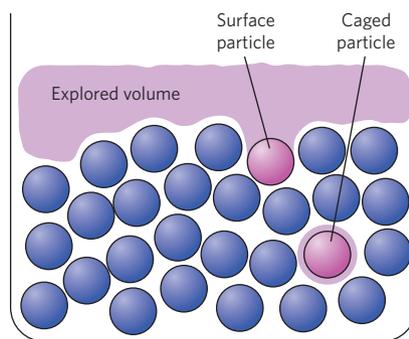
Now, Singh, Ediger and de Pablo report in *Nature Materials* that ultrastable glasses can also be reproduced by a computer

algorithm that mimics physical vapour deposition, and that these model glasses lie extremely low in the energy landscape<sup>5</sup> (Fig. 1). The algorithm, which is a modified molecular dynamics simulation, progressively introduces small groups of particles into the system while locally minimizing the potential energy and slowly reducing the temperature of the added particles. For years, scientists have struggled to devise algorithms capable of sampling the

regions of the energy landscape that lie close to the absolute minimum for disordered states. Singh and collaborators suggest that depositing particles from the vapour phase at the right conditions seems to be the most efficient way to sample the landscape's deepest basins. The authors also investigated the mechanism behind the formation of these model low-energy glasses at the single-particle level, unambiguously proving that a liquid layer does indeed exist on the surface of the deposited glass, and showed that particles in this layer are characterized by a mobility that is several orders of magnitude larger than that in the bulk. Importantly, they also show that the packing in these glasses is remarkably uniform (with regular Voronoi polyhedra abounding as structural motifs).

The statistical properties of the energy landscape close to its bottom, that is, the number and height distribution of the deepest basins, are intimately connected with the highly debated existence at low temperatures of a diverging correlation length in the glass. If no divergence exists, the free-energy barriers among the basins would always be finite and the potential energy would smoothly approach its low-temperature limit (Fig. 1, right). Yet if a diverging correlation length exists, the barriers become infinite at a non-zero temperature (the so-called Kautzmann temperature,  $T_K$ ). At this temperature the glass would reach the deepest basins and the derivative of the potential energy would display a discontinuity (Fig. 1, right). For temperatures lower than  $T_K$ , the system would then visit only the lowest energy basin, with a vanishing configurational entropy (the logarithm of the number of explored basins). This seems to be the case for the model glasses of Singh and colleagues, who noticed that the predicted  $T_K$  coincides with the optimal deposition temperature. Numerical and experimental tests of this result will surely come and, if confirmed, would provide strong support for the existence of a second-order thermodynamic transition at  $T_K$ .

Why is slow cooling significantly less efficient than (carefully designed) vapour



**Figure 2 |** Diagram of a vapour-deposited glass configuration. Particles in the bulk are caged by their neighbours and cannot significantly change their local environment within experimentally or numerically accessible time scales. Instead, particles in layers proximal to the free surface can diffuse within a much bigger region (pink) and explore the configuration space in search for the lowest energy states. Image courtesy of Lorenzo Rovigatti.

deposition at generating optimal glasses? In the bulk of a glass, the movement of each particle (be it an atom, molecule or polymer) is constrained by the cage formed by its neighbours (Fig. 2). Actually, the glass's structure is in effect frozen because at the temperature a glass exists, and on the typical scales of experimental (or numerical) observations, thermal vibrations are on average too low in energy to distort the cage and open an escape channel for the particle. For particles sitting on a free surface, instead, their average binding energy is significantly lower than it would be in the bulk and thus they are not confined in cages but can 'roll' on the surface without a significant free-energy cost. This enhanced mobility, which propagates within a few particle layers below the free surface, allows the particles to reach configurations that are more stable energetically before they become glassy as more particles are deposited on top. Hence, the presence of a free surface brings in a significant simplification to the complexity of the configuration space<sup>6</sup> and a reduction of the intra-basin energy barriers.

Further study of ultrastable glasses *in silico* may provide answers to questions in related fields. For example, will it be possible to elucidate the structure of the energy landscape close to the bottom, a topic connected to the long-debated existence of a truly thermodynamic transition underlying glass formation? For systems in which glass-glass transitions have been observed<sup>7</sup>, can vapour deposition at sufficiently high temperature resolve the ambiguities between equilibrium (ideal) and kinetically trapped glasses? Can strong network-forming liquids form even stronger glasses if they are vapour-deposited at optimal conditions? The debate on liquid-liquid transitions and their associated glasses in network-forming liquids (for example, water, silica and silicon) would benefit tremendously from answers to these questions. Also, it is known that crystals do not superheat because of surface melting, that is, the formation of a liquid layer at the gas/solid interface. Do ultrastable glasses melt in a similar way? Finally, we recall that efforts put into understanding spin and structural glasses have provided ideas and methodologies for other complex systems; for example, solutions to spin models have found application in random combinatorial problems and data compression<sup>8</sup>. Similarly, the algorithm of Singh and colleagues for accessing deep energy states in a complex energy landscape may end up making other optimization processes fly. □

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