Designing disordered materials beyond equilibrium

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A family of glassy materials emerges from local structural optimization, revealing an unexpected form of long-range orientational order.

Glasses are typically viewed as highly disordered materials. They are often described as having a frozen liquid structure, to convey both the absence of long-range structural order and the lack of molecular mobility. Sometimes the words 'random structure' are used to characterize atomic or molecular packings. From this perspective, the idea that a glass might display any form of order might seem counterintuitive. Yet, it has been known for nearly a century that equilibrating a glass-former at lower temperatures reduces its entropy relative to that of the corresponding crystal. Macroscopic thermodynamics therefore tells us that well-equilibrated amorphous solids must self-organize within a limited set of distinct packings. This suggests that some form of amorphous, or hidden, order develops in deeply equilibrated glassy materials. As new experimental and computational techniques allow access to glassy states located deep in the energy landscape and characterized by very low entropy, we now have an opportunity to identify and characterize the types of amorphous order that can exist in glasses.

Now, writing in *Nature Materials*, Ning Xu, Hajime Tanaka, Hua Tong and co-workers report a family of glasses obtained by numerically optimizing local particle packing[1]. These glasses exhibit a previously unexplored form of orientational order embedded within an otherwise amorphous structure. The authors study a two-dimensional system of nearly-hard disks with a broad distribution of diameters, a class of systems known to strongly resist crystallization and therefore well suited for investigating amorphous packings. Glassy configurations are first prepared using the swap Monte Carlo algorithm to reach very low energy states under conditions of thermal equilibrium. In a second step, a steric order parameter is optimized by allowing particle diameters to gradually adjust to locally improve the packing. Crucially, this second step lifts the constraints of thermal equilibrium. In the resulting packings, particles are in close contact with all their neighbours.

Optimizing steric order through the simultaneous dynamics of particle diameters and positions represents a novel design principle for glassy materials and leads to structures with striking properties. The resulting glasses display very low potential energy and high kinetic stability, as evidenced by an extended range of solid-like behaviour upon heating. They respond to mechanical deformation in an almost purely affine manner and show a near suppression of low-frequency localized vibrational modes. In each of these aspects, the observed behaviour is more extreme than that obtained through conventional cooling protocols, underscoring the strong impact of the non-equilibrium design procedure.

In addition to these features, Xu, Tanaka, Tong and co-workers report that their glasses display a new type of long-range orientation

correlation, as quantified by a path-integral-like approach. For context, we note that the literature contains many different ways of characterizing static and dynamic correlation length scales, and for the best-packed systems studied so far, the length scales identified are relatively modest, of the order of approximately 5–10 particle diameters[2]. The orientation correlation reported here is considerably longer-ranged. Understanding how this fits together with previous results is an important point for future work.

It is useful to place this study in the broader context of recent computational efforts aimed at optimizing packing in glasses (Fig. 1). Broadly speaking, these approaches fall into two categories. In the first, algorithms are designed to generate equilibrium configurations at the lowest achievable temperatures[3]. Because these methods preserve thermal equilibrium, they allow direct comparison with experimental systems. In the second category, equilibrium constraints are deliberately abandoned, opening the door to a wide range of design strategies. In such approaches, specific physical quantities can be directly optimized, as in the case of the steric order parameter considered by Xu, Tanaka, Tong and co-workers, without requiring the resulting state to be representative of an equilibrium ensemble. Clarifying the relationship between such non-equilibrium design protocols and equilibrium ones is therefore an important challenge.

Why does it matter whether highly packed amorphous states correspond to equilibrium configurations? For certain questions, equilibrium states are essential. They are required, for example, to understand the rapid loss of entropy upon cooling a supercooled liquid, to assess whether a true thermodynamic phase transition underlies the kinetic glass transition observed experimentally, and to test theoretical frameworks that are generally formulated for equilibrium systems. On the other hand, for real-world glassy materials, equilibrium is inconsequential, or even deleterious. Here the goal is to optimize a particular property or set of properties, and sometimes the best materials are clearly out-of-equilibrium. An interesting example is the glassy organic semiconductors used to produce light in smartphone displays. The glasses that produce the most efficient displays have anisotropic molecular packing[4], which is not a feature of the equilibrium state.

Using computer simulations to explore a broader set of design rules may lead to superior glassy materials that do not correspond to equilibrium states. An important next step is to understand how glasses produced by optimizing steric order compare with those obtained by optimizing other physical characteristics, such as hyperuniformity[5] or the distribution of local stresses[6]. Do different design strategies generate distinct families of non-equilibrium glassy states? To address this question, it will be necessary to introduce quantitative, universal metrics to compare the structures found in these materials independently of their preparation protocol. In addition, a complete and coherent understanding of the design rules themselves is needed. Some aspects are understood, for example, it is already known that annealing particle diameters and positions is sufficient to produce ultrastability[7], while
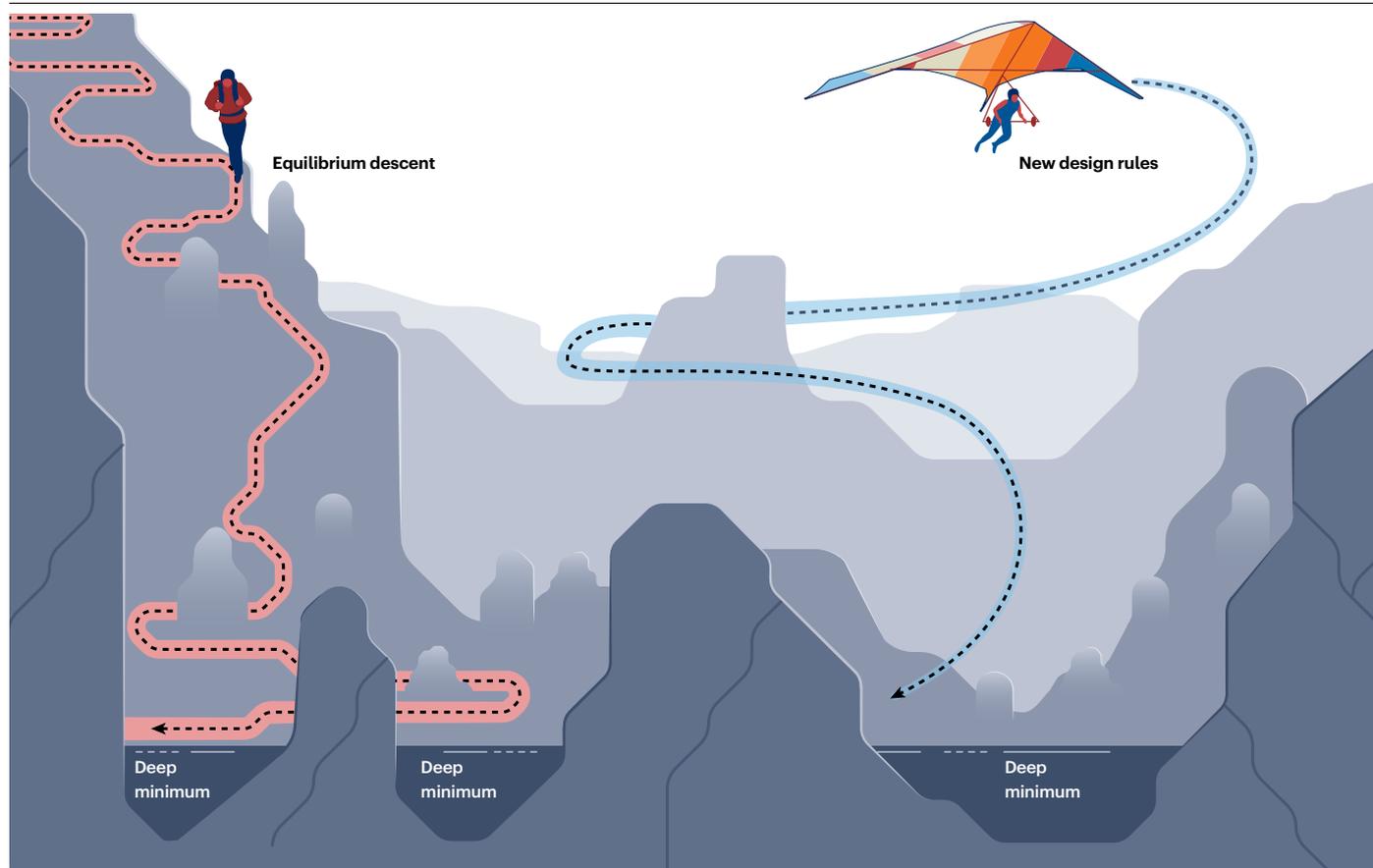
Fig. 1 | A schematic diagram of the potential energy landscape of glass-forming systems. In glass-forming systems, typical thermal equilibration methods require the system to follow a tortuous and difficult pathway to an energy minimum, akin to a gruelling hike. New design rules implemented in computer algorithms attempt to explore a broader variety of routes to the bottom by lifting constraints from thermal equilibrium, akin to a glider soaring over obstacles. These design rules potentially lead to amorphous materials that lie deep in the energy landscape and are endowed with distinctive structural properties.

crystal-like vibrational properties can emerge even when equilibrium constraints are employed[8]. Disentangling the various facets of the design protocols and understanding the causal relationship between optimizing a particular structural feature and the resulting macroscopic properties are exciting questions for future research.

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