

## DISORDERED MATERIALS

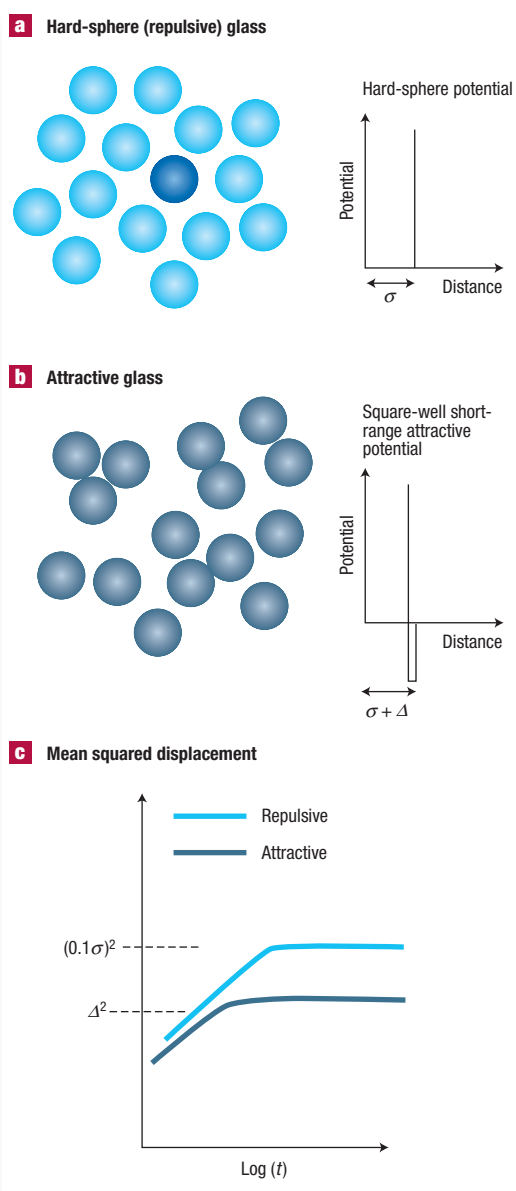
## One liquid, two glasses

The ability to tune the properties of disordered materials is reaching new levels. Experiments with colloidal systems, combined with theoretical predictions, may lead to the design of novel soft materials and to a deeper understanding of the glass and gel states of matter.

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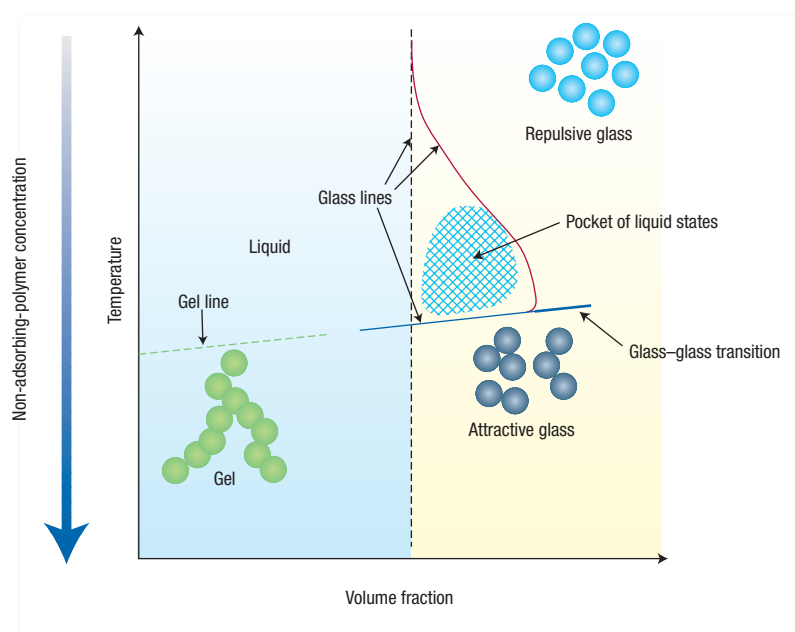
**W**hen liquids are cooled (or compressed) beyond the melting curve they usually crystallize. But, if crystallization is avoided, the dynamics of the liquid slow enormously. In such cases, the time required for a particle to travel a distance comparable to its size may grow by more than 15 orders of magnitude in a small temperature interval. Indeed, the motion of the particles may become so slow that the structure of the liquid—that is, the average positions of the particles—no longer changes. The liquid has undergone a so-called structural arrest and has turned into a disordered solid—a glass. The idea that structural arrest can also be achieved on heating is counter-intuitive, especially if observed in a liquid that also displays structural arrest on cooling. A recent article in *Physical Review Letters*<sup>1</sup>, and one earlier this year in *Science*<sup>2</sup>, provide experimental evidence that new materials can be designed so that a glass can be produced either by cooling or by heating the same material. This work moves predictions<sup>3,4</sup> based on the idealized ‘mode coupling theory’ (MCT)<sup>5</sup> from the realm of theoretical possibility to experimental fact.

The basic physics behind this fascinating phenomenon results from a competition between two different mechanisms constraining the particle motion. To grasp the origin of this competition, consider a very simple system composed of spherical particles that cannot get closer than a fixed distance,  $\sigma$  (Fig. 1a). Physicists call these particles ‘hard spheres’. When the volume occupied by the hard spheres becomes larger than 58% of the available volume, structural arrest is observed. In the resulting glass, particles are hindered from moving too much by the presence of neighbouring particles—caught like a passenger in an overcrowded bus during rush hour. Particles are said to be ‘caged’ by their neighbouring particles. Only an extremely rare collective rearrangement, for example opening a channel out of the cage, would allow for particle diffusion. In such packed conditions, particles can only rattle within their own cage, getting no further than an average distance of around  $0.1\sigma$ . Modern theories of the glass transition can explain this phenomenon for the hard-sphere case and provide estimates for the cage size that agree with observations<sup>5,6</sup>.



**Figure 1** Two simple models for the interaction between colloidal particles are the hard-sphere model and the short-range square-well potential. **a**, In the hard-sphere case, particles interact with an infinite repulsive potential when the interparticle distance is less than  $\sigma$ , to model the excluded volume effect. The darker blue sphere is clearly ‘caged’ by the surrounding spheres. **b**, In the short-range square-well potential, an attractive potential well follows the initial hard-sphere repulsion and a low-energy bond can be formed if the relative interparticle distance is between  $\sigma$  and  $\sigma + \Delta$ . When the fraction of volume filled by particles is large, structural arrest is observed and the particles are said to be localized in cages. Note that the short-range attraction, which forces particles to rattle within the potential well, generates larger void channels than the hard-sphere case. **c**, The average mean squared displacement is a measure of the average distance travelled by the particles and provides an estimate of the size of the cage. In the case of hard spheres this length is of the order of  $0.1\sigma$ , whereas in the case of the short-range attractive potential it is of the order of  $\Delta$ .

Now consider what happens in the presence of an additional short-range interparticle attractive interaction (Fig. 1b). At high temperature, the attraction does not play any role and, if the volume fraction occupied by the particles is large enough, the



**Figure 2** Temperature versus volume fraction phase diagram. The glass lines separate the 'liquid' regions, where particles are able to diffuse, from the 'glass' regions. The vertical black dashed line represents the hard-sphere glass line. In the case of short-range attractive colloids<sup>1,2</sup>, the re-entrant (non-monotonic) shape of the glass line (solid red and blue lines) creates a pocket of liquid states that are stabilized by the short-range attraction. The location of the theoretical glass–glass transition line (thick blue line) and the proposed connection between the gel-line (at low volume fractions) and the attractive glass line (solid blue line) are also indicated. Equilibrium (and metastable) lines between gas, liquid and solid phases — which in the case of attractive colloids are significantly different from the case of long-range attractions — are not shown.

material will behave pretty much like a hard-sphere glass. But if the range of the attraction,  $\Delta$ , is smaller than  $0.1\sigma$ , then, on cooling, particles will begin to stick together, effectively shrinking the confining cage size and producing a more inhomogeneous distribution of the empty space. As shown in Fig. 1b, these empty regions form channels through which particles can diffuse and so the material starts to melt. The glass has turned into a liquid on cooling! If the temperature is lowered further, interparticle bonding will become stronger and longer lasting, thereby restoring the usual progressive slowing down of dynamics, which results in another structural arrest. The liquid has turned into a glass.

In the phase diagram of temperature versus volume fraction (Fig. 2), this glass–liquid–glass sequence results in a re-entrant (non-monotonic) glass-transition line. It also means that some liquid states can be stabilized by the short-range attraction, and so — compared with the case of long-range attraction — the range of stability of the liquid phase is increased. It is important to stress here the differences with the case of polyamorphic materials where distinct glasses are predicted to exist as a consequence of the existence of distinct liquid phases. An example is the case of the amorphous forms of water which have been related to a metastable liquid–liquid critical point<sup>7</sup>.

In atomic and molecular systems, the range of attraction is always comparable to or larger than  $\sigma$  and thus the re-entrant phenomenon cannot be observed. But in new materials where the interparticle potential can be accurately controlled, this limitation is removed and extremely short-range potentials may be designed. For example, in a solution of globular proteins the interaction range can be controlled by changing the ionic strength. In sterically stabilized colloids, the attraction range can be tuned by changing the grafted chain–chain interaction<sup>8</sup>. In the system studied by Eckert and

Bartsch<sup>1</sup> and Pham *et al.*<sup>2</sup> — a mixture of colloidal particles and a non-adsorbing polymer — the length of the polymer fixes the interaction range and the amount of non-adsorbing polymer in solution fixes the interaction strength. Increasing the polymer concentration is equivalent to decreasing the temperature. So, together these studies provide compelling evidence that colloidal materials can form disordered solids both by increasing and by decreasing the polymer concentration.

New possibilities are expected to arise from further studies of colloidal systems with short-range attractions. The short-range bonding characteristic of the low-temperature (attractive) glass produces a much stiffer material than the one formed at high temperature (repulsive glass). By tuning the volume fraction and  $\Delta$ , it should also be possible to design a material in which the transition between the attractive and repulsive glass takes place without any intermediate liquid phase — that is, a glass-to-glass transition (Fig. 2). With a glass–glass transition, a small change in the external parameters could produce a remarkable change in the elastic properties of the material without any significant structural change. Theoretically, we can expect more than one order of magnitude change in the stiffness<sup>9</sup>.

Such phenomena have not yet been observed. But for materials scientists, the design, production and technological exploitation of such materials is one of the most fascinating opportunities presented by these studies<sup>1–4</sup>. In this respect, MCT calculations, whose predictive power has been significantly strengthened by the close agreement between predictions and experimental observation, might become a valuable instrument for guiding the design of novel soft materials with specific properties.

An additional point raised by studies on short-range attractive colloidal systems<sup>1–4</sup> is the possibility of applying these ideas to colloidal gelation and, more generally, to gel formation. Indeed, correlations between the dynamical behaviour of gels and glasses suggest that a common understanding of these two disordered forms of matter may emerge — once the different characteristic length-scales of gel-bonding and repulsive caging are accounted for<sup>10</sup>. In the case of attractive colloids, the sol–gel line would correspond to the low-density extension of the attractive glass line<sup>3</sup>. Future theoretical and experimental work focused on this stimulating idea may eventually provide a unified description of disordered phases of matter — as different as glasses and gels — within the same conceptual framework.

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