

Modern computational studies of the glass transition

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Abstract

The physics of the glass transition and amorphous materials continues to attract the attention of a wide research community after decades of effort. Supercooled liquids and glasses have been studied numerically since the advent of molecular dynamics and Monte Carlo simulations, and computer studies have greatly enhanced both experimental discoveries and theoretical developments. In this Review, we provide a modern perspective on this area. We describe the need to go beyond canonical methods when studying the glass transition – a problem that is notoriously difficult in terms of timescales, length scales and physical observables. We summarize recent algorithmic developments to achieve enhanced sampling and faster equilibration by using replica-exchange methods, cluster and swap Monte Carlo algorithms, and other techniques. We then review some major advances afforded by these tools regarding the statistical mechanical description of the liquid-to-glass transition, and the mechanical, vibrational and thermal properties of the glassy solid.

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Key points

- Simulations of glass-forming systems suffer from the rapidly growing relaxation times near the glass transition, which historically have limited simulations to the regime of very mild supercooling.
- A variety of methods, including simulated tempering methods and cluster Monte Carlo approaches, have been developed to deal with issues relating to slow equilibration.
- More recently, swap Monte Carlo methods, which augment standard local moves with swaps between particles that may be physically distant, have been shown to enable remarkably efficient equilibration in certain models of glass-forming systems.
- The equilibration speed-up afforded by swap Monte Carlo makes it possible to study glassy properties and behaviours that were previously out of reach, such as the nature of low-energy excitations in well-annealed glasses, and the brittle-to-ductile transition.
- Swap Monte Carlo has opened new vistas for the study of the behaviour of glassy systems, but new approaches for the simulation of dynamical behaviour as well as the equilibration of more complex glass-formers are still needed.

Introduction

A glass is a solid that is as mechanically stable as many crystals yet is completely disordered, bearing none of the structural hallmarks of ordered periodic crystals. Glasses are formed when a liquid can be rapidly cooled below its melting temperature, which typically leaves it in a liquid state. Further cooling of this liquid produces a glass¹. The cooling of a liquid to a glass spans approximately 15 orders of magnitude in relaxation time. This huge slowing of dynamics is accompanied by a host of features, such as highly collective and non-exponential dynamics referred to as dynamical heterogeneity², a non-Arrhenius temperature dependence of the viscosity, and stark violations of the Stokes–Einstein relationship³. The glass state itself differs in many ways from its crystalline counterpart, and a microscopic understanding of elementary excitations in the amorphous glass remains, perhaps surprisingly, an open problem.

The liquid-to-glass transition shares deep analogies with similar phenomena in other fields of science, such as those exhibited by some magnetic systems (like spin-glasses⁴), biological systems (in protein folding and misfolding⁵, for example), and in computer science (such as satisfiability problems⁶). Understanding the process of glass formation and the factors that imbue disordered solids with their unique properties is thus justifiably considered one of the outstanding problems of condensed matter.

From a computational viewpoint, this task is plagued by major obstacles, which include very sluggish dynamics, non-trivial finite-size effects, ergodicity breaking, strong sample-to-sample fluctuations and self-induced heterogeneity typically shared by other complex systems⁷. Computer simulations provide a powerful means to probe the microscopic details of the dynamics, structure and thermodynamics of supercooled systems as the glass transition is approached^{8,9}. However, such *in silico* experiments have historically been limited to small system sizes and the regime of very mild supercooling¹⁰. The latter limitation is

imposed by the fact that standard approaches require the local motion of particles to occur over temporal intervals that are much shorter than the time it takes the computer processor to carry them out, creating a bandwidth problem for slow dynamics. Thus, simulations of supercooled liquids have long been confined to approximately the first five decades of dynamical slow-down from the high-temperature liquid. This limitation makes it impossible to simulate phenomena close to the experimental glass transition temperature T_g (ref. ¹) or realistically study the glass itself.

In the past several years, rapid progress has been made on new algorithms that allow researchers to circumvent this timescale bottleneck and prepare glassy states that are effectively cooled as slowly as those prepared in the laboratory¹¹. These techniques may even allow simulation of glassy properties that are difficult to measure in real-world materials (such as growing static¹² and dynamical^{13–15} length scales close to the glass transition), provide the ability to study new phase transitions in glasses *in silico* (such as the brittle-to-ductile yielding transition^{16,17}) and afford the means to fill in the microscopic information absent from long-standing powerful but phenomenological theories (such as what actually tunnels in the two-level system model of Anderson, Halperin and Varma¹⁸ and of Phillips¹⁹). In this Review, we outline the key methods and the breakthroughs that made them possible, as well as the vistas that these techniques have opened on the nature of supercooled liquids and glasses.

Computational methods

Basic tools and glass-forming models

Computer simulations of glass-forming liquids use molecular dynamics or Monte Carlo techniques both to generate equilibrated configurations under specified thermodynamic conditions and to calculate dynamical trajectories from these configurations^{8,9}. Molecular dynamics aims to mimic the true classical microscopic motion of particles and is thus inherently local in terms of particle moves. When simulating realistic dynamics, Monte Carlo is also constrained to be local in its exploration of configuration space²⁰, otherwise it is complicated or even impossible to assign the timescale associated with particle moves²¹. However, when generating equilibrated configurations, Monte Carlo methods have the advantage that non-local and cluster moves may be used, with the potential for greatly accelerated exploration of phase space. Monte Carlo methods hence provide a more efficient generation of equilibrium configurations at high densities or low temperatures²². Both techniques require the specification of the form of an interparticle potential-energy function, as discussed below. Molecular dynamics simulations then proceed via the calculation of the force between particles from this function, whereas Monte Carlo requires only the potential energy itself, and except in specialized approaches such as force-bias Monte Carlo, does not generally require the calculation of forces.

Models of classical glass-forming systems can be crudely separated into three categories associated with the level of detail of the underlying description of the ‘particles’ and the interactions between them. The first category is that of realistic, off-lattice models of molecular glass-forming liquids. In these, the goal is to model the microscopic details of the interactions between the most common glass-forming substances such as glycerol or silica. The key component of such models is the form of the interaction potential or force field by which the atoms that form the molecules within the glass-forming liquid interact.

Even such models differ in their degree of realism and detail. For example, the van Beest–Kramer–van Santen (BKS) model of silica²³

is defined by a potential-energy surface that has been parametrized from a combination of *ab initio* and experimental data, and consists of Coulomb, Born–Mayer repulsive, and dispersive interactions between the Si and O atoms. Conversely, the Lewis and Wahnström model of the organic molecular liquid *ortho*-terphenyl replaces the entirety of each of the three benzene rings of the molecular unit with a single site that interacts with other sites with a simple Lennard–Jones potential²⁴. The latter case clearly involves some degree of atomic coarse-graining while retaining the non-spherical, albeit rigid, structure of the *ortho*-terphenyl molecular unit.

For all members of this category, simulating glass-forming behaviour is far more intensive than for either of the simpler categories described below. This is because the treatment of periodic systems composed of units with non-spherical shapes and rotational degrees of freedom, long-ranged interactions and other features poses complications for standard molecular dynamics and Monte Carlo simulations that render simulations more time-consuming than for simpler models where these features are absent⁸.

The models in the second category of *in silico* glass-formers describe simple systems of spherical particles interacting with short-ranged interactions. These systems may have a potential-energy function that is purely repulsive, such as the hard-sphere potential, or somewhat more complex interactions such as those described by the Lennard–Jones potential^{10,25,26}. Generally some degree of polydispersity and a tuning of the interactions are needed to prevent facile crystallization. Although the potential-energy functions for the models in this class may be used to describe experimentally relevant glass-formers, such as colloidal particles or some specific metallic glasses², the standard philosophy for their use is the fact that they demonstrate a nearly full range of non-trivial behaviours exhibited by more complex molecular glass-formers while being much more efficient to simulate numerically. In this sense, systems in this category form a middle ground between the complexity of the molecular systems discussed above and the fully coarse-grained models described below.

Finally, we come to models in the third category, which are fully coarse-grained lattice models. These models place particles on a lattice, with simple thermodynamic constraints imposed, such as restrictions on the number of neighbours allowed for a given particle type. There are no forces acting on particles, and dynamical evolution occurs via local Monte Carlo moves²⁷. These models, sometimes known as ‘lattice glass models’, generally suffer from a tendency to crystallize readily, although progress has been made in designing simple lattice models for which crystallization is strongly frustrated²⁸. The main utility of lattice glass models resides in the fact that they are simple enough to directly apply powerful mathematical techniques such as the replica method²⁹ for the calculation of thermodynamic properties to their lattice energy functions. They thus form a bridge between theories of the glass transition and more complex, off-lattice models.

In this Review, we largely focus on models in the second category. These models avoid both the complexity of molecular systems and the lack of realism of lattice models. They are realistic enough to be viewed as reasonable proxies for the simplest laboratory glass-formers such as metallic glasses, and thus we may view their study on the computer as *in silico* experiments on such systems. In particular, computer simulations aim to capture experimental behaviours such as violation of the Stokes–Einstein relationship, dramatically growing timescales, and the appearance of non-exponential and non-Arrhenius relaxation, which are shared by diverse molecular laboratory glass-formers and computer simulations of supercooled spherical particles with

short-ranged interactions. It is therefore reasonable to believe that little, if anything, of physical importance is being excluded by focusing on their study. Of course, properties specific to non-spherical degrees of freedom, such as the rotational version of the Stokes–Einstein relation or realistic modelling of dielectric relaxation, cannot be described by these models², and we do not discuss such properties here.

Equilibration tools in complex systems

A large portion of this Review focuses on simulation techniques used to generate equilibrated glassy samples. It is here that some of the biggest challenges exist for simulating glassy materials. Using local moves to produce equilibrated particle configurations is plagued by the timescale issues associated with dynamical slowing down. Increases in processor speed, even those afforded by newer architectures such as GPUs³⁰, are insufficient to enable the equilibration of samples anywhere close to the thermodynamic location of glass transition itself. Thus, tailored algorithms making use of non-local Monte Carlo and related techniques are necessary. It is also in these algorithms that the greatest recent progress has been made. This progress, together with the applications it has enabled, forms the core of this Review. Because relaxation timescales controlling particle motion change by many orders of magnitude as temperature decreases, an algorithmic speed-up of one or two orders of magnitude as often encountered below, although welcome, does not offer radical changes to the probed physics.

It is useful to sketch the history of the development of methods for equilibrating the Ising model³¹ and its cousins, such as binary alloys and spin-glass models²⁹. This illustrates the introduction of approaches to deal with slow equilibration issues, such as the slowing down near a critical point, as well as distinctions between the requirements for an efficient algorithm in these simpler models and those associated with the off-lattice problem of glassy liquids.

Standard single-spin-flip Monte Carlo approaches were first used to simulate the thermodynamics of the Ising model in 1953, soon after the introduction of the Monte Carlo algorithm³². These approaches encountered severe problems near the critical point, where equilibration timescale as a power of the growing length scale associated with emergent ferromagnetic order³³. Standard local Monte Carlo was also attempted around the same time to study order–disorder phenomena in binary alloy models. In 1959, non-local swap moves were introduced into the Monte Carlo framework for such systems^{34,35}. Interestingly, this approach took more than a decade to find its way into the study of off-lattice models of liquids, and several decades more to find applications in the study of glasses. As we discuss in this Review, a modern version of this idea, as embodied in the swap Monte Carlo (SMC) approach, has revolutionized the study of models of glass-formers belonging to the second class described above. In the next subsection, we discuss cluster and swap-based Monte Carlo techniques, but first we discuss an alternate route to accelerated equilibration.

In 1986, the replica Monte Carlo method was introduced to study the thermodynamics of Ising spin-glasses³⁶. Here, replicas of the system at different temperatures are simulated in equilibrium, with a partial exchange of configurational information allowed between replicas. A related but somewhat distinct and more general approach was put forward several years later^{37,38}, in the form of simulated tempering, which was used to investigate the random-field Ising model. In simulated tempering, a set of independent systems are simulated in equilibrium, with a Metropolis-like Monte Carlo exchange of temperatures between equilibrium configurations that maintains equilibrium (Fig. 1b). This class of Monte Carlo approach, also called

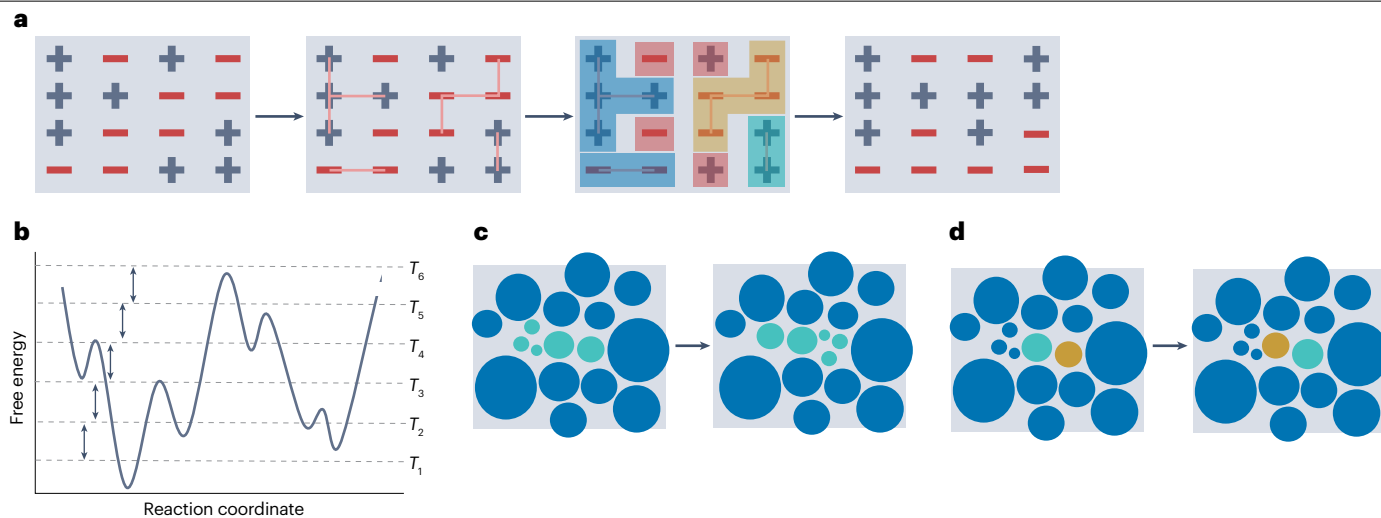


Fig. 1 | Sketch of various equilibration methods. **a**, Swendsen–Wang cluster Monte Carlo for lattice models, illustrated with a random-coupling Ising model in 2D. First, bonds are specified between like ‘up’ or ‘down’ spins depending on their coupling strength. Doing so defines clusters of spins that may be flipped with a Monte Carlo probability to yield an updated spin configuration²⁰⁵.

b, Parallel-tempering Monte Carlo. Monte Carlo calculations are run at different temperatures (six, in this case) and the temperatures or configurations exchanged, allowing for a more rapid sampling of phase space. **c**, A cluster move in the Dress–Krauth Monte Carlo algorithm⁶⁵. **d**, A swap Monte Carlo move.

parallel-tempering or replica-exchange Monte Carlo³⁹, has been of tremendous use in simulating complex systems with rough energy landscapes in fields from materials science to biology⁴⁰. For the study of bulk glasses, its performance is modest, although we will discuss important applications for which it is currently the most efficient method available.

Other methods for equilibrating and simulating lattice models have been investigated. Some of these methods appear fairly powerful. However, the use of these approaches for supercooled liquids has been sporadic and the results obtained for glassy systems somewhat anecdotal^{41–44}. Although these techniques merit further investigation, we do not discuss them further.

Enhanced sampling methods such as replica-exchange and related techniques have existed for several decades and have been applied successfully to sampling rough energy landscape problems in fields that bear some relationship to the glass transition problem, such as spin-glasses, the conformational equilibrium of polymers and biomolecules, and the screening of low-energy crystal structures⁴⁰. The situation is rather different for the study of glassy systems. To illustrate this, we first focus on the application of a molecular dynamics version of replica exchange, called replica-exchange molecular dynamics (RXMD), to equilibrate off-lattice supercooled liquid configurations⁴⁵.

RXMD has been explored in the binary Lennard–Jones Kob–Andersen model, perhaps the most ubiquitous of the second class of models as categorized above, following the protocol of ref. ⁴⁶ in the implementation of RXMD. In particular, M non-interacting replicas of systems of N particles each were used⁴⁵, where the Hamiltonian of each replica has its potential-energy function scaled by a constant parameter that acts as a means of controlling the temperature in the configurational average of the replicas. A constrained molecular dynamics simulation was then performed on the entire system comprising all replicas. Finally, the exchange of the scaling parameters (effectively an exchange of temperatures) between distinct replicas was considered

on a specified time interval, with acceptance rate governed by the standard canonical Metropolis criterion. This scheme is guaranteed to lead to canonical equilibrium at the set of temperatures of the replicas, and it reverts to standard molecular dynamics when no exchanges are attempted.

The efficient use of enhanced sampling techniques requires fine-tuning the algorithmic parameters. The abovementioned simulations used 16 replicas of $N = 10^3$ particles in a range in temperature from the onset of glassy dynamics to the mode-coupling crossover temperature T_c , covering approximately four decades of slowing down. The mode-coupling temperature marks the border of a regime where glassy behaviour becomes difficult to directly simulate in equilibrium via local molecular dynamics or Monte Carlo, even for present-day computers. As expected, the efficiency of the RXMD algorithm strongly depended on the exchange timescale, and was optimal for on the order of 10^3 time steps. Physically, this corresponds to the approximate timescale of oscillations of a particle trapped by its neighbours. Monitoring the effective diffusion constant of the particles showed that RXMD was up to 100 times more efficient at exploring phase space in the regimes studied, although equilibration below T_c was not attempted.

This approach was revisited in a simpler model of a one-component Lennard–Jones liquid with a term added to inhibit crystallization⁴⁷. The effective diffusion constant within replica-exchange-based approaches is controlled by the diffusion in the highest-temperature replica and carries little or no information on the equilibration rate. One can instead focus on the timescale to find the lowest local minimum in the potential-energy landscape⁴⁸. Within the purview of this more stringent criterion, using RXMD is not more efficient than standard molecular dynamics for equilibrating supercooled particle configurations.

Although others have also used variants of replica exchange or parallel tempering as a means to accelerate the sampling of equilibrium glassy configurations, these studies often combine the approach with other sampling techniques, making it difficult to isolate the role played

by the replica technique itself⁴². It is important to note that although RXMD, parallel tempering and related techniques do not seem to afford great increases in equilibration efficiency for bulk supercooled liquids, they do seem to provide the most efficient means of equilibrating supercooled liquids in confined geometries and in situations where a fraction of the particles are artificially frozen in place. Such situations are important for extracting growing static length scales as the glass transition is approached. These applications, and the power of replica-based approaches for studying them, will be discussed in the section on statistical mechanics analysis of glass transition.

So far, we have discussed computational tools that are widely used in different physical situations to study supercooled liquids. We close this section with two approaches that were proposed and developed specifically for glassy systems.

In 2007, it was discovered that amorphous films prepared using physical vapour deposition in well-chosen conditions had properties nearly equivalent to bulk glasses prepared at exceedingly small rates⁴⁹. After 15 years of detailed studies⁵⁰, it is understood that physical vapour deposition represents an experimental approach to accelerate the equilibration of supercooled liquids, with a speed-up that can reach many orders of magnitude. The physical origin of this observation is also understood: molecules arriving at the surface of the film have a much larger mobility than those already buried in the bulk. This enhanced surface mobility allows them to readily relax at temperatures at which the bulk is arrested. Motivated by this discovery, algorithms mimicking the deposition process were developed^{51,52}. However, on the timescales accessible to computer simulations, surface and bulk dynamics differ by at most one to two orders of magnitude, and the speed-up afforded by this method is much smaller than in experiments⁵³. In addition, simulating the growth process itself is not straightforward, and equilibration is not guaranteed. Therefore, simulating vapour deposition is useful to help interpret experimental studies⁵⁴ but is not a promising generic tool to speed up equilibration of computer glassy models.

The second method is more theoretically guided. It was initially developed to understand the nature of large deviations in the dynamic behaviour of glass-formers⁵⁵ as a way to describe more formally the nature of dynamic heterogeneity⁵⁶. Technically, the idea is to introduce a non-equilibrium sampling technique that biases the system towards dynamic trajectories exhibiting statistically rare properties, such as lower than average mobility⁵⁷. An outcome is the production of particle configurations that have physical properties that are different from the bulk and seem to lie deeper in the potential-energy landscape than equilibrium systems at the same temperature^{58–60}. There is ample evidence that these configurations represent very stable glassy configurations, but this has not been quantified. In addition, these tools do not scale well with system size, and they are currently limited to relatively small systems of at most a few hundred particles. However, the tools are promising, and their utility and performance remain to be more quantitatively established.

Cluster Monte Carlo and swap Monte Carlo

A powerful approach for simulating Ising-type systems close to criticality is the Swendsen and Wang cluster approach⁶¹, which involves using non-local, but detailed-balance-preserving, Monte Carlo cluster moves (Fig. 1a). This approach was initially illustrated in both the 2D Ising model and Potts models, where the critical slowing down associated with the second-order critical point is greatly mitigated by the algorithm's violation of dynamical universality, rendering a much less

severe space-time scaling exponent, which translates into a much more efficient algorithm when compared with standard single-spin Monte Carlo moves. Interestingly, as discussed below, the efficiency of the SMC algorithm manifests in a related manner in the simulation of glassy liquids. An analogue of the Swendsen and Wang cluster approach for simple off-lattice liquids and glasses⁶² is discussed in more detail below. The current limitation of cluster approaches for off-lattice models lies in the difficulty of efficiently determining and moving clusters. Doing so is a much more challenging task than in the Ising model, where, for example, the physics revealed by the knowledge of Fisher clusters⁶³ and the Fortuin–Kasteleyn⁶⁴ representation greatly simplifies the construction of the algorithm.

The pioneering work on spin models provided an impetus for the search for efficient cluster Monte Carlo approaches to accelerate the equilibration of particle-based glassy systems. This search led to a cluster approach (the Dress and Krauth algorithm) in which a copy of a particle configuration is rotated with respect to the original configuration as a means to identify clusters in the joint system via an overlap criterion⁶² (Fig. 1c). Each cluster can then be flipped around a pivot via a Metropolis procedure in which spheres belonging to one cluster are moved from the rotated copy back to the original configuration while those in the original configuration are moved to rotated copy. Such moves, in conjunction with simple single-particle Monte Carlo moves, satisfy detailed balance and can potentially accelerate the exploration of configuration space.

This cluster Monte Carlo approach was later used to study glass formation in a polydisperse hard-disk system in 2D⁶⁵. In this case, cluster Monte Carlo is more efficient than local Monte Carlo when judged by the reasonable criterion that the cluster approach enables the equilibration of configurations well past the mode-coupling density of the system, where a power-law fit of the diffusion constant would predict vanishing particle diffusivity. The authors⁶⁵ emphasize that even at the highest densities studied, their system displays no evidence of a change in thermodynamic quantities such as compressibility that could be interpreted as an equilibrium signature of a glass transition. However, the putative location of a thermodynamic transition for this system is unknown, and so these results merely prove that the mode-coupling transition does not correspond to a thermodynamic singularity. In any case, even in theories that purport the existence of a thermodynamic glass transition, such as the random first-order transition (RFOT) theory, such a transition is not expected to exist in 2D⁶⁶. As discussed further below, more recent simulations using SMC have provided stronger evidence that no signatures of a thermodynamic transition exist at finite temperature in 2D but that they do exist in 3D.

The cluster Monte Carlo algorithm has been used far less extensively than SMC, which we describe next. For simple systems of the second class of models, such as hard disks, it can be demonstrated that SMC is a more efficient algorithm⁶⁷. Some of the difference in the efficiency of these two approaches probably lies in the relative simplicity of the swap approach, which makes optimization substantially easier. In particular, the algorithm defined by Dress and Krauth merely defines one possible approach for isolating and exchanging clusters. Indeed, there are more general versions of the algorithm of Dress and Krauth, which have not yet been applied to glassy systems⁶⁸. It is likely that related algorithms could be devised that would exceed the capabilities of the Dress and Krauth approach, and that combining the cluster algorithm with other new sampling techniques could greatly enhance its efficiency. One example of work in this direction is

the use of the rejection-free event-chain Monte Carlo approach, which demonstrably enhances the sampling ability of cluster Monte Carlo^{69,70}. So far, for models of complex glass-forming liquids, the most powerful means of achieving deeper supercooling is via direct molecular dynamics simulation, making use of high-throughput methods⁷¹ or using advanced special-purpose hardware architecture such as Anton⁷². Thus, in our opinion, the search for such potential modifications is a worthy goal, given the somewhat circumscribed set of systems where SMC is extremely useful. Indeed, for extremely simple systems such as a monodisperse glass-former, SMC trivially affords no advantage, whereas for complex molecular liquids of the first class of models we have described, it seems to be fairly difficult to apply.

Above, we have casually compared the cluster Monte Carlo approach to the SMC method without formally defining the latter, mostly because the approach is nearly self-explanatory. Here, we touch upon the history of the approach, some details associated with its implementation, and the steps leading to its success as a means of generating deeply supercooled liquid configurations.

In the SMC algorithm, standard local Metropolis Monte Carlo is augmented with the potentially long-ranged swapping of pairs of particles (Fig. 1d). Optimization must be carried out with respect to the frequency of swapping trial moves and the range of particle sizes and types for which swap moves are attempted, but because all moves occur via the Metropolis criterion, the method is extremely simple and requires little tuning. In systems in which the approach is efficient, swap

moves may be rarely accepted, but when they are they can provide an enormous boost for equilibration. The degree to which the approach is useful depends sensitively on the acceptance rate of swap moves compared with local moves, which varies greatly between systems.

A variant of this type of Monte Carlo was used to study binary crystalline alloys a mere six years after the invention of the basic Monte Carlo algorithm itself³⁴. The first off-lattice use of SMC was in 1978, when the approach was used to investigate the structure and thermodynamics of relatively small binary Lennard–Jones clusters⁷³. In 1989, SMC was used to investigate the equation of state of non-additive hard-sphere mixtures⁷⁴. It thus took a full 30 years from the time of invention for the approach to be used to study bulk liquids.

In pioneering work, SMC was used to study the glassy behaviour of a 50:50 mixture of soft spheres⁷⁵. Although no detailed statements were made concerning the acceleration of equilibration over standard molecular dynamics or Monte Carlo, at high densities or low temperatures (these parameters are equivalent in soft-sphere systems) the inclusion of swap moves was found to render the algorithm much more efficient at reaching low-energy configurations on the energy landscape compared with both standard Monte Carlo and parallel tempering. For the soft-sphere system of 34 spheres, a rather stringent metric of equilibration – namely, the agreement between the specific heat as calculated from energy fluctuations and the temperature derivative of the average energy – holds for temperatures well below the expected location of the laboratory glass transition. This small system exhibits a broad maximum of the specific heat, which can be interpreted as the location of an entropy crisis. Extrapolation indicates a similar but sharper behaviour in an 800-particle system, with the location of the peak in the specific heat approximately agreeing with the predicted Kauzmann temperature as found from RFOT theory^{66,76}.

The status of the SMC approach to equilibrate supercooled particle configurations after this work remained unclear for several years. Here, two important studies stand out. In the same 50:50 soft-sphere mixture as studied in ref. ⁷⁵, SMC was shown to accelerate equilibration by approximately two orders of magnitude independently of temperature, a speed-up which is helpful but far from sufficient to study realistically annealed samples⁷⁷. In the polydisperse 2D hard-disk system of ref. ⁶⁵, SMC is more efficient than the pivot-based cluster Monte Carlo approach⁶⁷. However, less encouragingly, SMC was seen to suffer from a proclivity to crystallize all other systems under investigation, including 3D thermal analogues of the hard-disk system.

Perhaps because of these negative results, progress in the use of SMC stalled until 2017^{11,78}, when it was shown that if the interaction potential and the polydispersity of the sample are carefully tuned, amazingly efficient equilibration in large configurations is possible without signs of crystallization. The challenge was then to develop models for which swap moves are easily accepted, which can be achieved using either discrete mixtures in which swaps between different particle families can be performed, or continuously polydisperse systems. However, because such polydisperse models can easily crystallize, particle interactions must be carefully adjusted to prevent fractionation or phase separation, using, for instance, non-additive pair interactions. When these conditions are met, the efficiency of the approach is so high that one can easily reach and exceed the degree of annealing found in standard laboratory protocols (Fig. 2). In the intervening years, a host of model systems amenable to remarkably efficient equilibration via SMC have been devised^{11,79}. Recent work has also demonstrated that models of metallic glasses such as the venerable Kob–Andersen model⁸⁰, which mimics the NiP

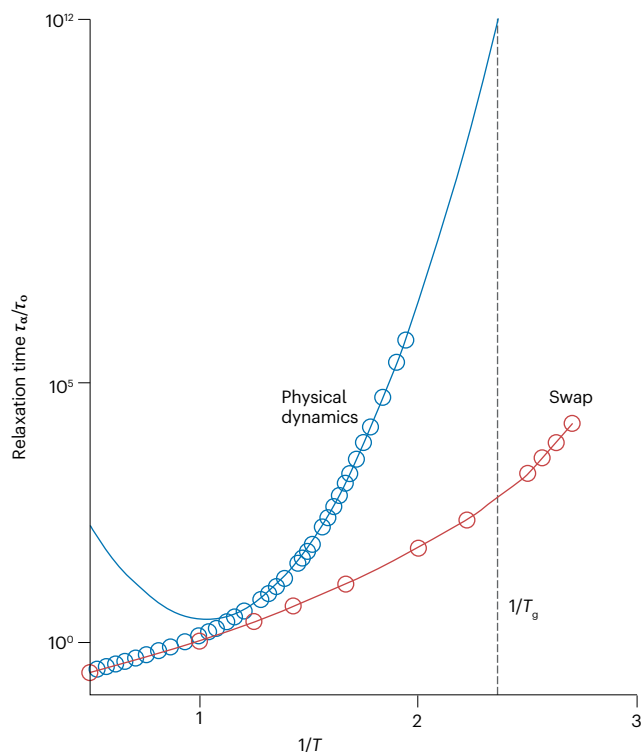


Fig. 2 | Speed-up of equilibration offered by swap Monte Carlo. Swap Monte Carlo (red) is compared with molecular dynamics (blue) for a 3D system of polydisperse soft spheres. The equilibration with swap Monte Carlo is about 10^{10} times faster at the experimental glass transition T_g and can be achieved below T_g to produce ultrastable computer glasses. T , temperature; τ_α , structural relaxation time; τ_0 , relaxation time at the onset of slow dynamics. Data from ref. ¹¹.

metallic glass-forming system, can be well approximated by a potential for which SMC can be efficiently carried out. This work has enabled a large number of previously impossible investigations into the properties of supercooled liquids and glasses in the second category of models as defined above. The remainder of this Review discusses this progress.

The performance demonstrated in Fig. 2, which represents a speed-up of a factor larger than 10^{10} at the experimental glass transition T_g , appears surprising in the context of advanced Monte Carlo techniques. In the cases discussed above, a computational bottleneck rooted in the physics of the problem was tackled using a technique originating from physical intuition. In the case of supercooled liquids, intuition suggests that because a rugged energy landscape controls the physics, methods such as parallel tempering should be favoured, but in fact these do not work well. The real-space view that associates slow dynamics to some form of spatial correlation between particles^{2,12} would instead suggest the need for collective cluster moves. In this second view, the success of SMC which introduces very basic two-particle moves is surprising. These considerations have led to several studies confronting the speed-up offered by SMC to the physics of supercooled liquids^{81–84}. Physically, the key is in the interplay between the translational degrees of freedom (particle positions) and the diameter dynamics introduced by the swap exchanges¹¹. The idea of augmenting the number of degrees of freedom has led to new algorithms that have proven useful in the context of the jamming transitions^{85,86}.

Advances in understanding the glass problem

Statistical mechanics analysis of glass transition

The equilibration speed-up afforded by SMC makes it possible to produce a large number of independent equilibrium configurations of a glass-former over a temperature regime that encompasses the experimental glass transition temperature. Doing so naturally provides a means to perform ensemble-averaged measurements of any equal-time correlation function and, by integration, any thermodynamic quantity of physical interest.

Since the landmark work of Kauzmann⁸⁷, the configurational entropy $S_{\text{conf}}(T)$ of supercooled liquids has played a special role in glass studies⁸⁸. Gathering available experimental data, Kauzmann provided estimates for the temperature dependence of S_{conf} and noticed a steep decrease as temperature decreases towards T_g . Extrapolating this evolution to temperatures below T_g where no experimental data are available, Kauzmann noted the possibility that a critical temperature, now known as the Kauzmann temperature T_K , could mark an entropy crisis with $S_{\text{conf}}(T \rightarrow T_K) = 0$.

Theoretical developments have since greatly clarified the conceptual, mathematical and physical contents of the configurational entropy⁸⁸. In the mean-field theory of the glass transition describing the physics of supercooled liquids in the limit of a large number of spatial dimensions, $d \rightarrow \infty$, a Kauzmann transition accompanied by a vanishing configurational entropy rigorously exists⁸⁹. In this framework, which serves as a basis for the RFOT theory⁹⁰, S_{conf} quantifies the complexity of a rugged free-energy landscape with a clear mathematical definition that does not involve any reference to a crystalline state.

It is not yet known whether a Kauzmann transition can exist in finite dimensions, $d < \infty$, but some key mean-field concepts are known to be greatly affected by finite-dimensional effects⁹¹. In particular, it is impossible to simply and rigorously define, let alone enumerate, long-lived free-energy minima in finite dimensions, and the mean-field definition of S_{conf} must be carefully reconsidered⁶⁶. Approximately 20 years ago,

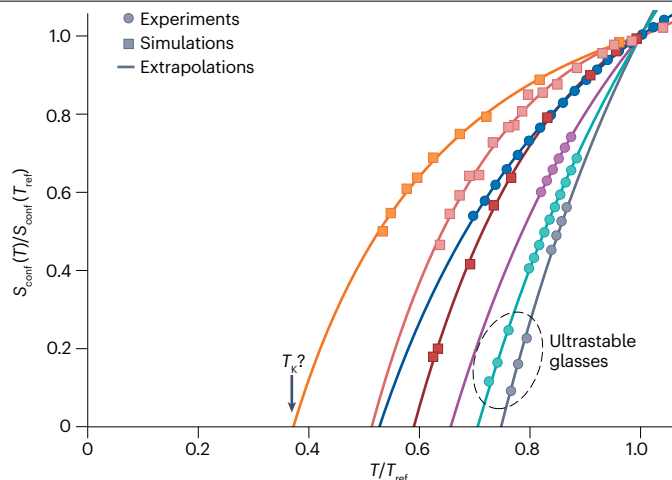


Fig. 3 | The evolution of experimental and numerical estimates of the configurational entropy offers a consistent view of the thermodynamics of 3D glasses. Experimental data include ultrastable thin films; numerical estimates are obtained using swap Monte Carlo. This data compilation revisits the famous plot first constructed by Kauzmann⁸⁷ for the excess entropy of molecular supercooled liquids. S_{conf} , configurational entropy; T , temperature; T_{ref} , high-temperature reference; T_K , Kauzmann temperature. Data are obtained from ref. 88.

a series of numerical works following older ideas^{48,92} introduced a definition of the configurational entropy based on potential-energy (rather than free-energy) minima^{93,94}. Although this was known to be an approximation, it permitted the development of explicit computational methods to obtain an estimate of $S_{\text{conf}}(T)$ that has been used across a wide range of models. A strong limitation to these early efforts is the narrow temperature range covered by these measurements, which is mostly above the mode-coupling crossover temperature and corresponds, within the RFOT theory, to a regime where S_{conf} cannot even be defined.

The situation changed after 2017 when the SMC algorithm opened a path to analyse the thermodynamic properties of supercooled liquids at, and even below, T_g . At the methodological level, new methods were developed to provide computational estimates of S_{conf} that are conceptually much closer to the rigorous theoretical definition of this quantity^{95,96}; in practice, these measurements could now be performed in the temperature regime where theory predicts the validity of S_{conf} and experimental estimates exist. This new generation of measurements was performed across a range of simple models of spherical particles with short-range interactions (the second category described above) in both 2D and 3D⁸⁸.

The first result from these measurements is that the steep decrease of $S_{\text{conf}}(T)$ reported by Kauzmann is recovered in all models⁹⁷ (Fig. 3). This result is not trivial, given the diversity of molecules analysed in Kauzmann's work and the different nature of the quantity he reported. It also confirms in particular that no reference to the crystalline state of the material is needed to estimate S_{conf} . More quantitatively, extrapolating the numerical data to temperatures where even SMC is unable to provide equilibrated configurations suggests that a finite Kauzmann temperature $T_K > 0$ can exist in 3D models⁹⁷, whereas a different behaviour is found in 2D where extrapolations seem to suggest that $T_K = 0$ (ref. 98). These findings are in line with RFOT theory, which implies that

the Kauzmann transition should be destroyed by finite-dimensional fluctuations in $d \lesssim 2$.

These measurements, together with theoretical developments, give additional insight into the nature of the putative Kauzmann transition. Within the mean-field description, the entropy crisis at T_K corresponds to a first-order change between a metastable glass phase above T_K and an ‘ideal’ glass phase below T_K with vanishing configurational entropy. For $T > T_K$, which is the regime explored in equilibrium conditions, the glass phase is metastable with respect to the liquid, and the configurational entropy can be interpreted as the free-energy difference between the two phases⁹⁹. This insight has two interesting consequences for simulations. First, it provides a computational path⁹⁵ to estimate the configurational entropy by using free-energy calculations of the type developed to analyse conventional phase transitions⁸. Doing so typically requires measuring large deviations in the fluctuations of the order parameter; methods such as umbrella sampling are well suited for such tasks, and they can be readily adapted to the case of supercooled liquids¹⁰⁰.

A second consequence of the glass metastability just above T_K is the possibility of inducing a discontinuous phase transition towards the glass phase by application of a thermodynamic field that favours the glass, usually denoted ε (ref. 99). Doing so amounts to adding a new dimension to the equilibrium phase diagram of supercooled liquids. In this extended phase space (T, ε) , the Kauzmann transition signals the liquid–glass phase change when $\varepsilon = 0$, but a discontinuous first-order transition line $\varepsilon(T)$ emerges from the Kauzmann point for temperatures above T_K . This line ends at a second-order critical point (T_c, ε_c) , which RFOT theory predicts should lie in the same universality class as the random-field Ising model⁹¹. From an experimental viewpoint, these considerations may appear as formal theoretical developments. However, they are directly amenable to quantitative numerical tests, a programme that was started in the late 1990s^{101,102}. These initial studies turned into quantitative tests only after SMC was developed.

A complete exploration of the (T, ε) phase diagram, together with finite-size scaling analysis of the corresponding phase transitions, is now available^{103–105}. These studies confirm the existence of a first-order transition line in the regime $T > T_K$ for 3D glass-formers, and scaling analysis confirms the universality class of the critical end-point¹⁰⁴. In 2D models, no critical end-point is found, in agreement with studies of the random-field Ising model itself, and scaling analysis again demonstrates good agreement with a zero-temperature Kauzmann transition¹⁰⁵.

Overall, these thermodynamic results are strong hints that the random first-order transition theory of the glass transition provides an accurate description of the static properties and thermodynamic fluctuations in supercooled liquids. However, similar fluctuations and behaviour can be generically expected in systems displaying growing static order, such as multispin plaquette models¹⁰⁶, which also exhibit constrained phase transitions¹⁰⁷ but are devoid of any finite-temperature Kauzmann transition.

Because the Kauzmann transition is discontinuous, no critical fluctuations of an order parameter are expected to grow as T_K is approached from above, even in the mean-field limit. Therefore, the search for growing length scales as a sign of emerging order is more complicated for glasses than it is for simpler types of phase transformations. Generally speaking, the length scale that grows in the vicinity of a first-order transition is a nucleation length scale, usually defined as the critical size that a nucleus of the stable phase must have in order to destabilize the metastable one⁸. In the context of the glass transition, this analogy has been used to rigorously define¹⁰⁸ the corresponding length scale, now

called the point-to-set length scale. A practical algorithmic procedure was also proposed¹² to measure the point-to-set length scale. Since the free-energy difference between glass and liquid phases above T_K is directly related to S_{conf} , the point-to-set length scale is expected to be inversely proportional to this free-energy driving force given by S_{conf} , which would possibly diverge at T_K , where the entropy vanishes.

This algorithmic construction works as follows. The positions of all particles outside a spherical cavity are frozen in an equilibrium configuration to impose the glass metastable phase outside the cavity. Particles inside the cavity instead evolve freely, and can eventually relax (thus returning to the liquid phase) when the cavity size becomes larger than the critical nucleation radius. By monitoring the typical state of the interior of the cavity as a function of the cavity size, a characteristic point-to-set length scale can be measured numerically^{109–111}. However, in practice, particles inside the cavity are so strongly constrained by the frozen boundaries that it is difficult to probe their thermodynamic properties even with SMC. An additional equilibration effort involving parallel tempering is needed to properly measure the point-to-set length scale⁷⁸. The agreement with the temperature evolution of S_{conf} was confirmed^{97,112}, directly demonstrating how a decreasing entropy, a growing point-to-set length scale and a decreasing free-energy difference between glass and liquid all reveal the proximity to a Kauzmann transition and can be detected in simulations of bulk equilibrium supercooled liquids.

In the past decade, the idea of freezing the positions of a set of particles has been investigated in various geometries¹¹³, in addition to the closed cavity used to infer the point-to-set length scale. For example, freezing the position of particles in a half space creates an infinite wall of frozen particles that acts as an interesting geometry to detect correlation length scales^{114–116}. Another example is when a finite fraction c of particles chosen at random is frozen from an equilibrium configuration¹¹⁷. In that case, the system remains globally isotropic and spatially homogeneous, but the frozen particles considerably reduce the size of the available configuration space. In the mean-field limit, it can be rigorously shown that this reduction induces an entropy crisis of similar nature to the temperature-driven Kauzmann transition¹¹⁸. As for the frozen cavity, the constraint imposed by this random pinning procedure makes it difficult to properly estimate thermodynamic properties of the remaining free particles, and parallel tempering has been used to study this situation. Evidence was provided that a sharp change happens as c is increased at constant temperature, which seems consistent with an incipient phase transition¹¹⁹, accompanied by a steep decrease of the configurational entropy¹²⁰. In the future, lower temperatures should be studied and a rigorous finite-size scaling analysis should be conducted to fully establish that this situation truly corresponds to an equilibrium Kauzmann transition.

Rheology of amorphous solids

We now turn to the rheological properties of the glass state, which is a topic of practical and experimental interest^{121,122}. Computer simulations are well suited to analyse the glassy rheology of dense colloidal suspensions because the timescales that can be explored experimentally and numerically using conventional numerical methods coincide well. The analysis of steady-state flow curves for materials undergoing large deformations represents an important research area¹⁶.

By contrast, atomic and molecular glass-formers cannot be arbitrarily deformed because they break or fracture at large deformations. Therefore, one is led to analyse the elasticity of the glass in the linear response regime and the initial plasticity of the deformed material, which is possibly followed by macroscopic failure, often taking the

form of a macroscopic shear band in which the plastic deformation is almost entirely localized.

As usual, computer simulations are a priori severely limited in such an endeavour¹²³. A first issue is the typical rate at which the material is deformed, which is larger by many orders of magnitude in standard molecular dynamics than that which can commonly be reached in a real mechanical experiment. This problem was solved about 20 years ago by the introduction of a tool called athermal quasistatic deformation, which alternates incremental deformation steps and global energy minimization^{124–126}. In this approach, the effective rate of deformation is zero, and this particular timescale issue is completely solved, although thermal fluctuations are then neglected.

A more problematic issue is that computer simulations can only study the mechanical properties of configurations that are prepared numerically via some cooling protocol. Over the past two decades, computer simulations have therefore analysed the mechanical properties of molecular glasses quenched to the glass state with cooling rates that are approximately 10^8 times faster than in conventional experiments, resulting in poorly annealed glassy states. Such systems

can readily support large deformations and very much behave as soft colloidal glasses: that is, the yielding of the glass occurs as a smooth crossover to a flowing state as a function of deformation. This mode of yielding is typical of ductile materials and has been carefully analysed in many simulation works¹²⁷.

The advent of the SMC algorithm radically changed the situation, as the preparation of glassy configurations with effective cooling rates equivalent to those used for real molecular glasses became possible. By using the athermal quasistatic protocol for models of glass-formers similar to earlier work, it was shown in 2018¹²⁸ that increasing the initial stability of the glass was sufficient to change the yielding behaviour from ductile (as observed in earlier simulations) to a brittle yielding accompanied by a macroscopic failure of the material, as seen in experiments. The tendency to localize the plastic deformation more strongly in space had been found to increase slowly as the preparation time of the system increases¹²⁹. However, for the very stable configurations analysed in ref. ¹²⁸, finite-size scaling analysis shows that macroscopic failure happens suddenly in a single deformation step, in a way that fluctuates less in larger systems (Fig. 4). This result

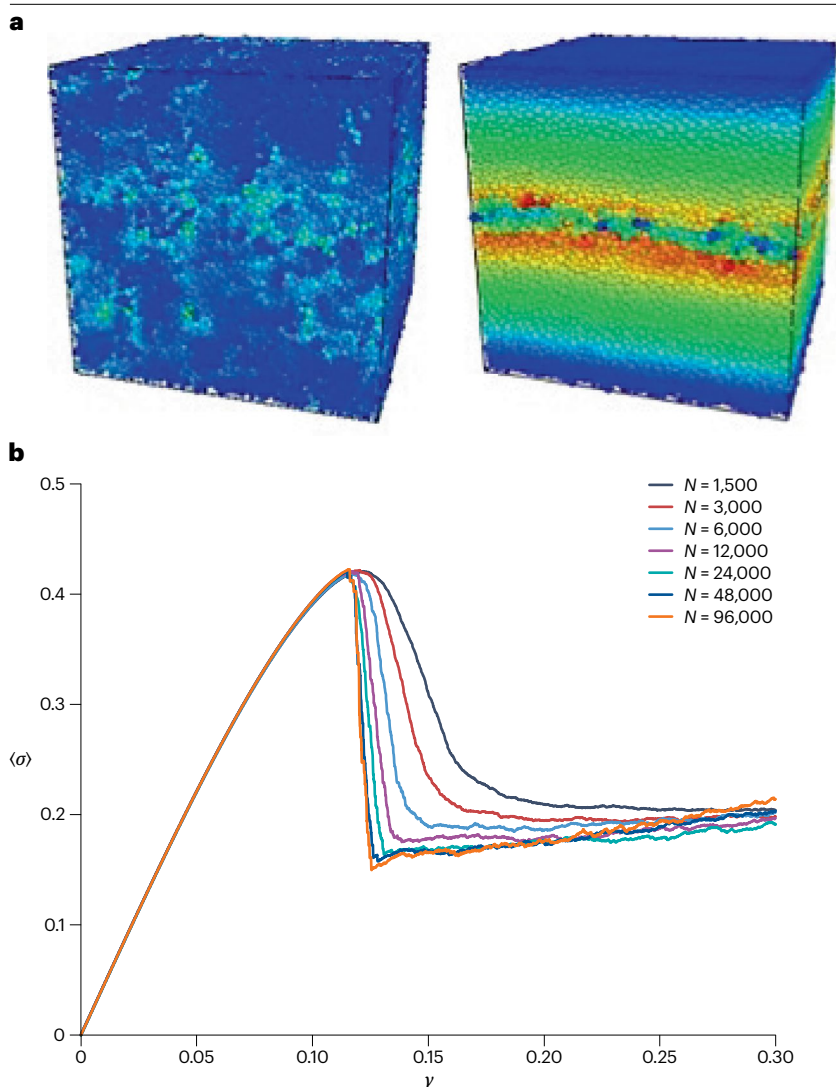


Fig. 4 | Brittle yielding of computer glasses via computer simulations. **a**, Ductile yielding in a poorly annealed material (left), and brittle yielding in a stable material (right). Particle colours indicate the amount of plastic deformation in the deformed material at the yielding transition. **b**, Brittle yielding in a stable glass, provoking a sharp and discontinuous macroscopic discontinuity in the stress–strain (σ – γ) relation in the thermodynamic limit. N , number of particles. Figure adapted with permission from ref. ¹²⁸, PNAS.

is compatible with the view that yielding in very stable glassy states can be described as a kind of discontinuous non-equilibrium phase transition. This finding echoes both theoretical developments, in which yielding is treated in the realm of statistical mechanics^{130,131}, and experimental results showing that real glasses break abruptly via brittle macroscopic failure.

This initial work¹²⁸ paved the way for several research directions. In the initial study, the numerics suggested that the clear discontinuous yielding transition observed for very stable glasses becomes less discontinuous and slowly transforms into the smooth crossover observed for ductile materials. On the basis of these results, complemented by the analytical solution of a mean-field model for yielding, it was suggested that the brittle-to-ductile yielding transition could itself be described by a second-order critical point with universal properties similar to those of a random-field Ising model¹²⁸. Further work in 2D glasses¹³² supports this picture, but concerns were later raised about possible finite-size effects^{133,134}. Future work using off-lattice and coarse-grained models¹³⁵, together with theoretical developments, will hopefully clarify the nature of the brittle-to-ductile transition.

A second line of research concerns variations of the geometry and timescale for the deformation. The case of periodic deformation, which represents an important class of mechanical tests in industrial applications, has been analysed in depth^{136,137}. In addition, the influence of a finite rate of deformation on brittle yielding was studied¹³⁸. Finally, having at hand realistic glass samples, there is hope that a platform to understand in detail the microscopic nature of the plastic events leading to stress relaxation in amorphous solids is now available^{139,140}. Additional studies should also address the effect of thermal fluctuations.

Vibrational and thermal properties of glasses

The solid-state properties of glasses hold many mysteries that can now be convincingly addressed with the advent of *in silico* preparation of well-equilibrated configurations. These features include the unusual properties of the vibrational density of states in a disordered solid^{141–146}, and the putative role played by localized tunnelling states on the energy landscape, which become operative at cryogenic temperatures^{18,19} (Fig. 5).

It has long been appreciated that configurational disorder induces qualitative changes in the behaviour of the low-energy eigenstates of the vibrational Hessian matrix that quantifies quadratic fluctuations around a glass minimum^{145,147,148}. In particular, in addition to the plane-wave phonon modes expected from continuum elasticity, modes with localized behaviour, dubbed ‘quasilocalized’ modes, appear in the vibrational spectrum (also called the density of states), $D(\omega)$. The contributions of both extended and quasilocalized modes to $D(\omega)$ render its behaviour distinct from the Debye spectrum expected for simple ordered solids.

As the system size increases, a separation of the modes in the low-frequency wing of $D(\omega)$ into extended and quasilocalized modes becomes gradually apparent¹⁴⁹. A focus on the contribution of the extended modes to the spectrum reveals an excess peak (the ‘boson peak’ visible at some finite frequency when plotting the density of states rescaled by the Debye contribution), which then merges with the expected Debye behaviour at much lower frequencies, namely $D_{\text{ex}}(\omega) \sim \omega^{d-1}$, as $\omega \rightarrow 0$ (ref. ¹⁵⁰). At sufficiently low temperatures, the quasilocalized contribution to the spectrum surprisingly takes a different functional form, $D_{\text{ql}}(\omega) \sim \omega^4$, with the exponent independent of dimensionality^{145,149,150}. These observations can be

rationalized theoretically and are visible, to a lesser extent, in poorly annealed samples.

The advent of SMC has made it possible to confirm these features in well-equilibrated samples of relevance to real experiments performed on amorphous solids. Perhaps more importantly, the use of SMC has pinpointed which features evolve as a function of the annealing rate. Specifically, the core of quasilocalized modes becomes more localized in better annealed configurations^{149,151}. Concomitantly, the prefactor of the quartic law associated with the density of states of the quasilocalized modes decreases rapidly as the degree of annealing increases¹⁴⁹. The ultimate fate of these features for even lower quench rates remains an open question.

At ultralow temperatures near 1 K, the thermodynamic properties of glasses markedly and quasi-universally deviate from those of crystals. In particular, the specific heat of a glass in this temperature range is much larger than in its parent crystal and shows a nearly linear, as opposed to cubic, temperature dependence¹⁵². Given the vibrational properties of amorphous solids discussed above, such behaviour seems surprising, because the contribution of quasilocalized modes in excess to Debye does not account for the specific heat data. A successful explanation for the thermodynamic properties of glasses in this regime comes from the phenomenological two-level system theory of Anderson, Halperin and Varma¹⁸, and of Phillips¹⁹. This theory posits

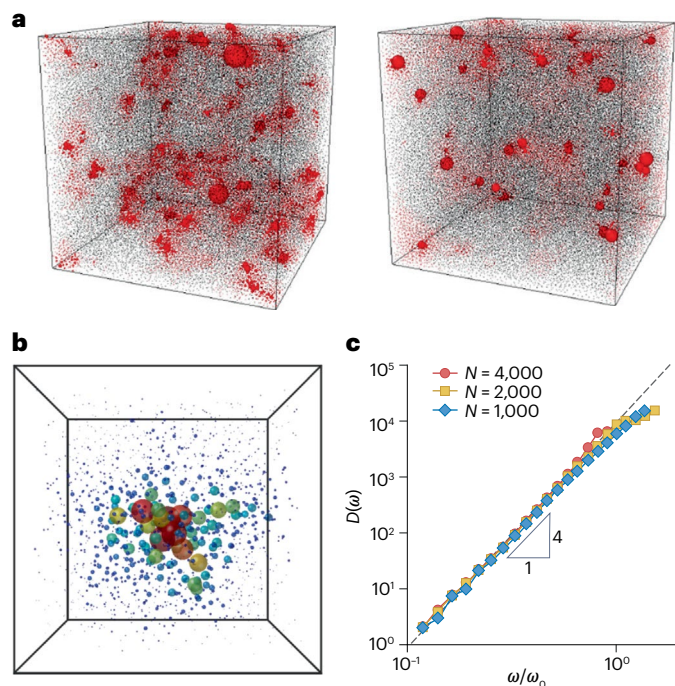


Fig. 5 | Low-temperature properties of glasses. **a**, The ‘softness’ field obtained from summing the real-space character of low-frequency modes for two different quench rates, where increasing size indicates increasing softness. The configuration on the right (slower quench) illustrates the smaller number of quasilocalized modes with a higher degree of localization. **b**, A rare, highly collective tunnelling event in a simulated glass, where size and colour indicate the amplitude of the particle displacements. **c**, The density of states $D(\omega)$ of vibrations in a 3D amorphous solid, illustrating the ω^4 behaviour at low frequency, ω . N , number of particles; ω_0 , microscopic frequency scale. Panel **a** adapted from ref. ¹⁴⁹ under a Creative Commons licence [CC BY 4.0](https://creativecommons.org/licenses/by/4.0/). Panel **b** adapted with permission from ref. ¹⁶⁰, APS. Panel **c** adapted with permission from ref. ¹⁵⁰, APS.

that local configurations in glasses can tunnel between two configurations, and the ensemble of these tunnelling defects provides an excess set of excitations that explains the glass anomalies.

Attempts to test this theory *in silico* and thus reveal the microscopic nature of local defect modes in glasses date back to 1993¹⁵³. In small ($N=150$) systems with a binary potential-energy function that was created to mimic an amorphous mixture of nickel and phosphorus¹⁵⁴, standard molecular dynamics equilibration techniques revealed several hundred pairs of local minima separated by a single barrier¹⁵³. However, only a single such double-well potential had a tunnelling splitting of the order of 1 K. This difficulty necessitated the use of an indirect extrapolation technique to infer the distribution of tunnelling levels in the range where the two-level system model is expected to be operative. Regardless, these early results conform closely to the predictions of the two-level system model.

In the decades since this pioneering work, its approach has been extended and used to study other glass-forming systems^{155–159}. Unfortunately, limitations in algorithms and hardware have meant that computer simulations have produced an incomplete picture of low-energy excitations in glasses. In addition to small system sizes, the lack of an approach such as SMC has heretofore meant that amorphous systems unrealistically prepared *in silico* have been studied.

The advent of SMC provided an impetus to revisit the goals of the original studies. SMC has been used to investigate the local structure of the lowest energy states of the energy landscape of a polydisperse soft-sphere glass as a function of the degree of equilibration, ranging from poorly annealed systems to those that are as well equilibrated as laboratory ultrastable glasses^{160,161}. Efficient protocols can locate connected minima and find the lowest-energy pathways between them. This approach has enabled the direct extraction of a large number of tunnelling systems even under the most well-equilibrated conditions. In turn, this has afforded a direct test of the two-level system model, revealing that the distribution of tunnelling systems is in agreement with that proposed by Anderson, Halperin and Varma, and by Phillips. In addition, the density of tunnelling systems decreases sharply as the stability of the glass configurations increases, as observed in many (but not all) experiments on ultrastable glasses^{162–164}. The vast majority of tunnelling systems are associated with local defect-like motion, but rare, highly collective, tunnelling motion occasionally occurs, especially in more poorly annealed systems (Fig. 5c).

Many unanswered questions remain with respect to the non-phononic excitations discussed above. SMC is limited in the range of potential-energy surfaces for which it can provide substantial equilibration efficiency gains. Thus, the origin of the intriguing experimentally observed quasi-universality in various ratios of material constants associated with two-level systems in starkly different glassy systems remains unexplored by computer simulation¹⁶⁵. The connection between two-level systems and quasilocated modes – a connection that is central to the phenomenological soft-potential model^{166,167} – demands more attention, despite some recent work along these lines¹⁶⁸. A rigorous, multidimensional treatment of tunnelling on the potential-energy landscape has yet to be carried out¹⁶⁹. Finally, a precise, quantitative means of calculating the density of tunnelling systems in simulated glasses is lacking, because protocols to search the energy landscape that are required to gather a statistically significant sample of two-level systems differ from the experimental quench pathway taking in the laboratory. These and other issues should be addressed in future work.

A surprising outcome of the large- d statistical mechanics approach to the glass transition is the prediction that the glass phase itself is not unique but can undergo a transition between two types of glassy states characterized by distinct physical properties¹⁷⁰. This Gardner transition had first been discovered in the context of mean-field spin-glass models¹⁷¹, and its prediction in the context of structural glasses has led to intense research activity in recent years¹⁷². From a computational viewpoint, SMC played a pivotal role in this endeavour because the predicted transition occurs when adiabatically following very stable glassy states that only SMC can achieve. Clear signs of a phase transition have been reported in 3D hard-sphere glasses^{173–175}; the transition becomes a strong crossover in 2D hard disks¹⁷⁶. The phase behaviour of soft glasses is more subtle¹⁷⁷, and the Gardner transition does not seem to occur in more conventional glass-formers such as Lennard–Jones systems¹⁷⁸. This behaviour shows that more work is needed to fully assess the problem of the Gardner transition in generic glass-formers.

Outlook

From a fundamental perspective, the glass problem has gone through important transformations in recent years, as theoretical, computational and experimental progress has paved the way towards a better understanding of some key issues. We believe that this progress will help to organize the field around well-posed questions that can directly be addressed analytically or numerically. We close this Review by describing some research directions that we think will see important progress in the coming years.

One nascent direction of research stems from the ongoing revolution created by the systematic application of deep learning techniques to many areas of physical science. The glass transition has also been attacked by various machine learning techniques to address various questions. One important line of research, which is somewhat peripheral to this Review, is the use of machine learning tools to develop interaction potentials between glass-forming atoms and molecules that have an *ab initio* level of accuracy¹⁷⁹, thus making important progress towards the development of better models in the first category of models described above.

A second line of research involving machine learning pertains to the development of methods to detect, in an unsupervised manner, the existence of important structural properties in glassy configurations that may otherwise appear devoid of structural heterogeneity^{180,181}. The goal is to use deep learning techniques to automatically detect, with no *a priori* bias, the geometric motifs that may be relevant to understanding the thermodynamic evolution of glass-formers. The hope is that machine learning can outperform existing attempts to detect relevant structural motifs in supercooled liquids that are based on physical intuition^{182–184}.

Finally, a related but distinct investigative thrust is the application of machine learning techniques to probe the fundamental question of how the structure of a supercooled liquid encodes the heterogeneous slow dynamics arising from a given initial configuration. Proposed approaches to predict the structural propensity for dynamics on different timescales include simple metrics, such as the softness field which relies on training local dynamics to local structural pair correlation functions¹⁸⁵, and more complex approaches such as the use of graph neural networks¹⁸⁶. Current efforts try to develop the best architecture to improve the quality and the simplicity of predictions, while simultaneously improving on the list of structural indicators used as inputs¹⁸⁷. The overall goal would be both to make extremely accurate predictions in order to draw some physical conclusions from them,

and to extract from the learned models what the structural descriptors are that correlate best with the long-time dynamics. Given the pace at which machine learning techniques are propagating throughout many computational areas, we expect to see much more activity in this area. These approaches have, in particular, great potential to allow for a detailed mechanistic understanding of how the structure (such as local packing motifs), which appears remarkably similar to that of the high-temperature liquid state that it was cooled from, encodes the strikingly heterogeneous dynamics that is the hallmark of supercooled liquids. Similar questions are being asked in the context of deformed glasses where plasticity is typically also very heterogeneous in space and time^{139,188}.

There are also a number of open questions that are awaiting the development of better simulation techniques. Techniques such as SMC work remarkably well for systems that mimic metallic glass-formers, but the simulation of glasses composed of the more complex family of molecular glass-forming liquids is currently out of reach via any Monte Carlo approach. Can generalized versions of cluster Monte Carlo methods be invented to simulate such systems? Doing so would help to answer the important question of how universal the underlying microscopic dynamical motifs are in a diverse class of glass-forming systems. The many new results concerning the physical behaviour of simple point-particle models near the experimental glass transitions have not yet been confirmed in more complicated but experimentally more typical models. Although there is hope and there are theoretical reasons that a fair degree of universality will eventually be found, it is necessary to develop the numerical tools to confirm this hypothesis. Doing so would then allow researchers to close the remaining gap between simulations and experiments. We believe that extended versions of the SMC could first be attempted in the simplest known models of molecular glasses, such as systems comprised of coarse-grained molecules or short polymeric chains.

Progress using computer simulations to directly determine the thermodynamic fluctuations and extended phase diagrams of supercooled liquids near the glass transition has demonstrated that the framework of RFOT theory, which stems from the firm basis of the mean-field theory of the glass transition, appears to correctly describe the thermodynamics of 2D and 3D glass-formers. However, the strong hints of an underlying Kauzmann transition remain subject to a temperature extrapolation, because it remains impossible to equilibrate to temperatures close enough to T_K to directly observe the transition. It could be that the SMC is too primitive an algorithm to approach T_K because it represents, after all, only a simple variation upon canonical Monte Carlo simulations for fluids. We may surmise that the development of smarter Monte Carlo algorithms that possibly displace several particles at once, perhaps in conjunction with parallel tempering, would be needed to approach the Kauzmann transition closely enough to directly observe the entropy crisis and firmly test the validity of RFOT theory.

Connected to this question, there is a pressing need to develop approaches that may, perhaps in a coarse-grained manner, enable simulation of the long-time dynamics of supercooled liquids close to the glass transition. Over the past decade, progress has been made in creating dynamical strategies^{189–192}, correlation functions^{14,15} and tools^{193,194} to assess and describe crucial aspects of glass formation, such as dynamical heterogeneity and growing dynamical length scales.

Some of these tools are expensive to simulate via molecular dynamics even at relatively high temperatures. For example, the quantity $S_4(\mathbf{q}, t)$, which is a four-point function from which growing

dynamical length scales can be extracted^{14,15}, requires not only a large degree of ensemble averaging but also large system sizes to extract accurate dynamical exponents¹⁹⁵. The advent of techniques such as SMC enables the creation of glassy samples that are annealed in a realistic manner beyond the capability of local Monte Carlo or molecular dynamics. However, simulating the direct long-time dynamics from such configurations remains a difficult task for highly annealed systems because the dynamics themselves span many orders of magnitude in time. The use of advanced Monte Carlo methods to create initial conditions for simulations on dedicated specialized hardware such as Anton can only partially overcome this problem⁷². Although SMC has helped to enlarge the time window that can be analysed numerically^{196–198}, future effort must be focused on this most crucial of questions.

In our view, a remaining unexplored territory is the dynamics of deeply supercooled liquids in the temperature regime pertinent to experimental work. Although measured thermodynamic fluctuations tend to agree with the RFOT theory description, this gives no guarantee that relaxation dynamics directly follows from the thermodynamics in the manner envisaged by theory^{12,66}, or, more broadly, that it is controlled by features encoded in the potential-energy landscape^{199,200}. There are several indications that dynamics may be controlled by a small population of localized defects^{201,202} and that contributions to the long-time dynamics come from purely dynamic relaxation channels that are not readily described by thermodynamic quantities, such as dynamic facilitation^{198,202–204}. We expect that the development of new algorithms, together with improvement in molecular dynamics implementations, will provide the tools to numerically study the long-time dynamics of glassy liquids near the experimental glass transition.

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The authors declare no competing interests.

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