Statistical physics of the glass phase

Marc Mézard

*Laboratoire de Physique Théorique et Modèles Statistiques, Université Paris Sud, Bat. 100,
91405 Orsay Cedex, France*

Abstract

This paper, prepared for the proceedings of the 'Statphys 21' conference (Cancun, July 2001)
gives an introduction to the statistical physics problems which appear in the study of structural
glasses. It is a shortened and updated version of a more detailed review paper which has appeared
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Under a rapid enough cooling, almost any liquid becomes a glass [1,2]. This is a
state of matter in which the density profile, as observed on accessible time scales, is
not flat as in a liquid, it contains some peaks as in a crystal, but these peaks are not
located on the nodes of a periodic or quasi periodic lattice. Particles tend to localize
around some fixed positions, which appear random.

Glasses have been recognized for their technological importance for several millenia,
and a large proportion of matter in nature is found in a glass state. But they also
offer a wonderful set of theoretical questions, most of which are very far from being
understood.

The first such question which comes to mind is whether the glass is a new state
of matter, or whether it is just a liquid state where the relaxation to uniform density
has become so slow that it is inobservable. The question is difficult because the glass
state is not distinguished by any obvious symmetry (a not-obvious symmetry will be
discussed later) from the liquid state. A similar problem was studied in the context
of spin glasses, which also undergo a transition from a paramagnetic 'liquid' state to
a state where the spins are frozen in random directions. In spin glasses, experiments
have provided convincing evidence for the existence, at least in zero magnetic field, of
a critical temperature where the non-linear part of the magnetic susceptibility diverges
with well defined critical exponents. Thus the experiments on spin glasses tend to

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E-mail address: mezard@physique.ens.fr (M. Mézard).

favour the existence of a phase transition and of a new spin-glassy state of matter
[4]. This behaviour is also found in the study of mean field theories [5], and recent
simulations on some model three dimensional spin glasses also point in this same
direction, but there does not exist any proof of the transition in any finite dimensional
spin glass model: a challenge to mathematical physics!

Similar challenges, but much more difficult, exist in the study of structural glasses
[6], and one may fear that relevant rigorous results will not be found in the near
future. Let us examine how one can formulate the problems of structural glasses from
a restricted statistical physics point of view. One wants to start from a microscopic
Hamiltonian. The simplest situation is that of N point-like particles in a volume V:

$$H = \sum_{i<j} V(r_i - r_j), \qquad (1)$$

with a pair interaction potential $V(r)$ which can be for instance either a hard sphere
potential, a 'soft sphere' potential ($V(r) = A/r^{12}$), or a Lennard–Jones potential ($V(r) = A/r^{12} - B/r^6$). Because these systems tends to crystallize even on the short time scales
accessible numerically, one often uses [3] the binary mixtures where there are two
types of particles A, B, and three different interaction potentials $V_{AA}(r), V_{BB}(r), V_{AB}(r)$.

Here is a small sample of questions one would like to ask on these systems, from
a statistical physics point of view.

- '*Equilibrium*' *questions*:
  Given the interaction potential, is there a true phase transition to a new state of
  matter? Is there a transition nearby in parameter space, which is never seen, for
  instance because it is in an unphysical region of parameters, or because the time
  scales make it impossible to reach the transition? Does there exist some choice
  of the V's such that the crystal is frustrated enough, in such a way that the true
  equilibrium state below some temperature is actually a glass state? Does there exist
  at least some choices where the glass state exists as a long-lived metastable state
  (like the diamond phase of carbon)? Is there a generic geometric description of the
  glass transition in terms of potential energy landscape, or of free energy landscape?
  What is the role of geometric frustration, the role of dimension?
- '*Dynamical*' *questions*:
  Do these 'equilibrium' questions (or more precisely the answers to them) have any-
  thing to do with the experimentally observed processes of extreme slowing down
  upon decrease in temperature, or with the out of equilibrium dynamics observed
  in the glass phase? Are there more universal descriptions of systems falling out of
  equilibrium, which are common to some systems having a glass transition and others
  being always (slow) liquids? How does the choice of the interaction potential, and
  the corresponding energy landscape, affect the dynamics and the glass transition?

These questions are just meant to point out that glasses offer some basic challenges to
statistical physics, on top of all the challenges they also offer from different perspectives
like chemistry and material sciences.

One should not forget either that some type of glassy states are often encountered in
many different fields outside of physics, and progress in the study of glass phases has

already brought new results in many different areas such as combinatorial optimization [5,7], error correcting codes [8], or behaviours of interacting agents [9]. In fact one often encounters in these fields some problems which are simpler than those of the glass phases found in nature, because there is no spatial structure: the interaction between various 'atoms' (constraints, agents, etc.) typically takes place between randomly chosen atoms, without a constraint of spatial neighbourhood. This allows for some exact solutions using mean field like methods.

Turning back to structural glasses, even if one forgets about rigorous mathematical proofs, I must say that all of the above questions are unanswered: there are some hints of answers coming from experiments, simulations, theories on simple systems, mean field theories, etc., and the progress in the last few years is real, but there is no real consensus around one single and consistent scenario. Let us see some pieces of this puzzle.

Experimentally, when crystallisation is avoided, a supercooled liquid falls out of equilibrium on experimental time scales, [1] and becomes a 'glass', at a temperature T_g called the glass temperature [2]. This glass temperature is conventionally defined as the one at which the relaxation time τ of the liquid, as obtained e.g. from viscosity or from susceptibility measurements, becomes of the order of 10^3 s. Angell's plot of $\log(\tau/1s)$ versus T_g/T allows to distinguish several types of behaviour. So called strong glasses like SiO_2 have $\log(\tau/1s) = A(T_g/T)$, a typical Arrhenius behaviour with one well defined free energy barrier. On the other hand, some glasses, called fragile, show a dramatic increase of the relaxation time when decreasing temperature which is much faster than Arrhenius: the typical free energy barrier thus increases when T decreases.

A popular fit of the relaxation time versus temperature is the Vogel Fulcher one,

$$\tau \sim \tau_0 \exp\left(\frac{A}{T - T_{VF}}\right) \tag{2}$$

which would predict a phase transition at a temperature T_{VF} which is not accessible experimentally (while staying at equilibrium). The more fragile the glass, the closer is T_{VF} to T_g, while strong glass formers have a T_{VF} close to zero. The increase of barrier heights when T decreases in fragile glasses might imply a collective behaviour involving more and more particles, however no sign of a divergent static correlation length has been found so far (an increasing dynamic length has been found recently [10]).

Another much studied property is the specific heat. When one cools the liquid slowly, at a cooling rate $\Gamma = -dT/dt$, it freezes into a glass at a temperature which decreases slightly when Γ decreases. When this freezing occurs, the specific heat jumps downward, from its value in the equilibrated supercooled liquid (see footnote 1) state to a glass value which is close to that of the crystal. This is a signature of the fact that the system below the freezing temperature is non-ergodic on experimental time

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[1] Of course there is always an ambiguity due to the existence of the crystal. In good glass formers, the nucleation time for the formation of the crystal becomes so huge at the temperatures close to T_g that one can forget about the existence of the crystal phase: although there is no such phase as an 'equilibrated supercooled liquid phase' in principle, it exists in practice, when the ratio of crystallisation time to equilibration of the liquid is very large.

scales. From the specific heat, one can compute configurational entropy, defined as the difference $S_c = S_{liq} - S_{crystal}$. It decreases smoothly with T in the supercooled liquid phase, until the system becomes a glass. It was noted by Kauzmann long ago that, if extrapolated, $S_c(T)$ vanishes at a finite temperature T_K. If cooled more slowly, the system follows the smooth $S_c(T)$ curve down to slightly lower temperatures, but then freezes again. One can wonder what could happen at infinitely slow cooling. As a negative S_c does not make sense (except for pure hard spheres, where there is no energy), something must happen at temperatures above T_K. The curve $S_c(T)$ could flatten down smoothly, or there might be a phase transition, which in the simplest scenario would lead to $S_c(T) = 0$ at $T < T_K$. This idea of an underlying 'ideal' phase transition,[2] which could be obtained only at infinitely slow cooling, receives some support from the following observation: the two temperatures where the *extrapolated* experimental behaviour has a singularity, T_{VF} and T_K, turn out to be amazingly close to each other [11]. The first phenomenological attempts to explain this fact originate in the work of Kauzmann [12], and were developed among others by Adam et al. [13], which identifies the glass transition as a 'bona fide' thermodynamic transition blurred by some dynamical effects.

If there exists a true thermodynamic glass transition at $T = T_K = T_{VF}$, it is a transition of a strange type. It is of second order because the entropy and internal energy are continuous. On the other hand the order parameter is discontinuous at the transition, as in first order transitions: the modulation of the microscopic density profile in the glass does not appear continuously from the flat profile of the liquid. As soon as the system freezes, there is a finite jump in this modulation (a more precise definition of the order parameter will be given below).

It turns out that such a 1st–2nd order type transition has been found in the theoretical study of some mean field models for a certain category of spin glasses. A few years after the replica symmetry breaking (RSB) solution of the mean field theory of spin glasses [5], it was realized that there exists another category of mean-field spin glasses where the static phase transition exists and is due to an entropy crisis [14]. These are now called discontinuous spin glasses because their phase transition, although it is of second order in the Ehrenfest sense, has a discontinuous order parameter [15]. An alternative name is 'one step RSB' spin glasses (because of the special pattern of symmetry breaking involved in their solution) and the new type of transition is sometimes named a 'random first order transition'.

The archetypes of discontinuous spin glasses involve infinite range interactions between triplets (or higher order groups) of spins. The simplest among them is the random energy model, which is the $p \rightarrow \infty$ limit version of the p-spin models described by the Hamiltonian

$$H = - \sum_{i_1 < \cdots < i_p} J_{i_1 \cdots i_p} s_{i_1} \ldots s_{i_p} \tag{3}$$

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[2] Sometimes the term 'ideal glass transition' is also used to characterize the mode coupling temperature. However in many systems we know for sure that there is no transition at the mode coupling temperature, and I prefer to use this term as describing the putative transition taking place at T_K.

where the J's are (appropriately scaled) quenched random couplings, and the spins can be either of Ising or spherical type [15–17]. The analogy between the phase transition of discontinuous spin glasses and the 'transition' in structural glasses was first noticed in the mid-eighties [16]. While some of the basic ideas of the present development were around at that time, there still missed a few crucial ingredients.

One big obstacle was the existence (in spin glasses) versus the absence (in structural glasses) of quenched disorder. The discovery of discontinuous spin glasses without any quenched disorder [18–20] provided an important new piece of information: contrarily to what had been believed for long, quenched disorder is not necessary for the existence of a spin glass phase. In fact it has been found recently that some suitably defined systems can self induce disorder and frustration in their dynamical behaviour, even if these properties are not present in the system a priori.

Here I would like to mention one such system, which displays some properties strikingly similar to structural glasses, and can be studied in great details. This example is a purely ferromagnetic $p = 3$ spin model of the type (3). The spins s_1, s_2, s_3 around a plaquette interact with a ferromagnetic term $-Js_1 s_2 s_3$. If the plaquettes are organized in a Bethe lattice of plaquettes where each spin belongs to exactly k plaquettes, one has no disorder on any finite lengthscale, and no frustration (the ground state is unique and purely ferromagnetic: all spins up). One can in fact solve this problem completely [21]. There exists a ferromagnetic phase, but it is very difficult to find it dynamically, and instead the spins tend to freeze into a glass phase (see Fig. 1). The reason is easy to understand: if the spin s_1 has a wrong orientation ($s_1 = -1$), the plaquette interaction induces an effective *antiferromagnetic* interaction between s_2 and s_3, and the system is thus frustrated, and disordered, unless it has found its exact ferromagnetic ground state $s_i = 1$. Similar interesting 'plaquette' model have been described in three dimensions, and studied numerically [22].

A closer look at the solution of a discontinuous spin glass problem such as the one in Fig. 1 shows that there are actually two transition temperatures. There is a true equilibrium transition at a temperature T_K, with a jump downward of the specific heat. However there also exists a dynamical transition temperature at a temperature T_c which is larger than the equilibrium transition T_K. When T decreases and gets near to T_c, the correlation function relaxes with a characteristic two steps form: a fast β relaxation leading to a plateau takes place on a characteristic time which does not grow, while the α relaxation from the plateau takes place on a time scale which diverges when $T \to T_c$ (see Fig. 2). This dynamic transition is exactly described by the schematic mode coupling equations [23,24]. The presence of this two steps relaxation is a well known experimental fact in structural glasses, and a lot of work has shown that many observed details of this two times relaxation are well characterized by the mode coupling theory, provided one does not get too close to T_c. However, mode coupling theory would predict that the relaxation times diverges at T_c, where experiments clearly find a finite relaxation time. From the point of view of discontinuous spin glasses, the existence of a dynamic transition is associated with the fact that the system can be trapped in metastable states with an extensive excitation free energy above the equilibrium state. This is possible only in mean field. In finite dimensions, nucleation effects (called activated effects in the mode coupling literature) prohibit such a situation. An important
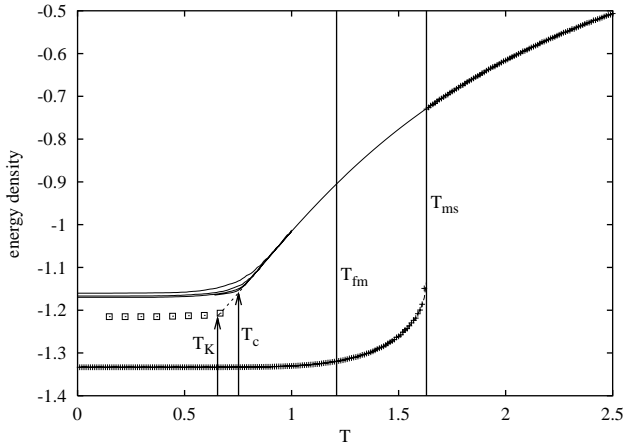
Fig. 1. Average energy as a function of the temperature for the ferromagnetic triangular plaquette model, on a Bethe hyperlattice where each spin belongs to $k = 4$ plaquettes (from Ref. [20]). If one prepares the system at low temperature in its ferromagnetic configuration $s_i = 1$, and heats it up, the energy follows the bottom curve. At temperature T_{fm} the ferromagnetic state becomes metastable, but the system stays in this metastable ferromagnetic state until the spinodal temperature T_{ms} is reached. It then becomes paramagnetic. Cooling down from the paramagnetic state, the energy follows the upper curve, where the magnetization is zero. Below T_{fm} one is in a regime of supercooled paramagnetic state. In the temperature range below 0.9, one sees the effects of the cooling rate dependance on the energy (cooling rates from 10^2 to 10^5 MCS per $\Delta T = 0.01$). The theory predicts that at infinitely slow cooling there is a dynamical transition at T_c, where the energy is blocked at a threshold value, while the equilibrium ideal glass transition takes place at T_K, and the equilibrium energy density below T_K is given by the squares. It is conjectured that in finite dimensional models the temperature T_c marks the onset of activated processes: the energy can decrease slowly, and the real transition takes place at T_K.

conjecture [16] is that in a realistic system like a glass, the region between T_K and T_c will have instead a finite, but very rapidly increasing, relaxation time, as explained in Fig. 2. A similar behaviour has been found in finite-size mean field models [25].

Another very interesting dynamical regime is the out of equilibrium one ($T < T_g$). Then the system is no longer stationary: it ages. Schematically, new relaxation processes come into play on a time scale comparable to the age of the system: the older the system, the longer the time needed for this 'aging' relaxation to take place. Recent years have seen important developments on the out of equilibrium dynamics in glassy phases [26], initiated by the exact solution of the dynamics in a discontinuous spin glass [27]. It has become clear that, in realistic systems with short range interactions, the pattern of replica symmetry breaking can be deduced from the measurements of the violation of the fluctuation dissipation theorem [28]. These measurements are difficult. However, numerical simulations performed on different types of glass forming systems have provided an independent and spectacular confirmation of their 'one step RSB' structure [29–32] on the (short) time scales which are accessible. Experimental results have not yet settled the issue, but the first measurements of effective temperatures in the fluctuation dissipation relation have been made recently [33]. One should also
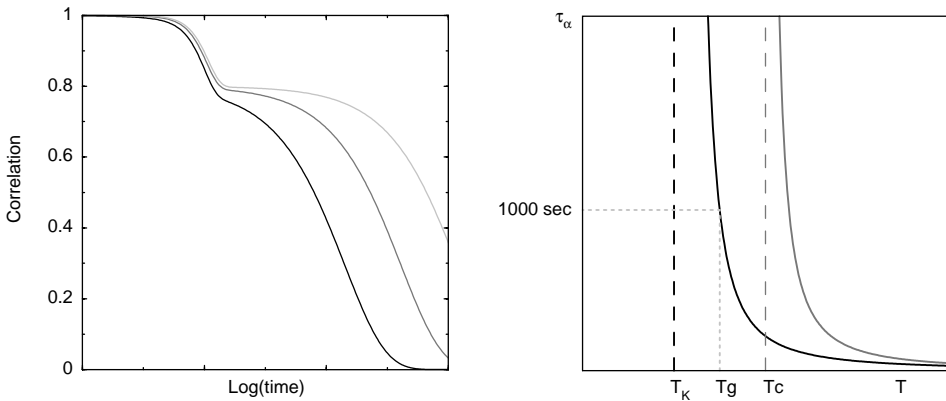
Fig. 2. The left-hand figure shows the schematic behaviour of the correlation function found in mean field discontinuous spin glasses and observed in structural glasses. The typical two-step relaxation consists of a fast β relaxation leading to a plateau, followed by a α relaxation from the plateau, whose typical time scale increases rapidly when T decreases, and diverges at $T = T_c$ which is equal to the mode-coupling transition temperature. The right-hand figure shows the behaviour of the relaxation time versus temperature. The right-hand curve is the prediction of mode-coupling theory without any activated processes: it is a mean field prediction, which is exact for instance in the discontinuous mean-field spin glasses. The left-hand curve is the observed relaxation time in a glass. The mode coupling theory provides a quantitative prediction for the increase of the relaxation time when decreasing temperature, at high enough temperature (well above the mode coupling transition T_c) [22,23]. The departure from the mean field prediction at lower temperatures is usually attributed to 'hopping' or 'activated' processes, in which the system is trapped for a long time in some valleys, but can eventually jump out of it. The ideal glass transition, which takes place at T_K, cannot be observed directly since the system becomes out of equilibrium on laboratory time scales at the 'glass temperature' T_g.

underline that the concepts of effective temperature goes beyond the restricted field of glasses and is being currently tested on various problems like granular media [34].

To summarize, the analogy between the phenomenology of fragile glass formers and discontinuous mean field spin glasses accounts for:

- The discontinuity of the order parameter.
- The continuity of the energy and the entropy.
- The jump in specific heat (and the sign of the jump).
- Some kind of 'entropy crisis' à la Kaufmann (see below).
- The two steps relaxation of the dynamics and the success of Mode Coupling Theory at relatively high temperatures.
- The aging phenomenon and the pattern of modification of the fluctuation dissipation relation in the low temperature phase.

Because of the successes of the above analogy, it is worth to study the basic ingredients at work in the glass transition of the mean field discontinuous spin glasses. At temperatures $T_K < T < T_c$, the phase space breaks up into ergodic components which are well separated, so-called free energy valleys or TAP states [35]. This has been confirmed recently by some rigorous implementation of the cavity method [36]. Each
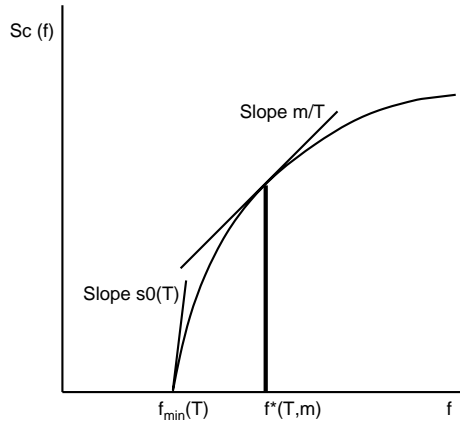
Fig. 3. Qualitative shape of the complexity versus free energy in mean field discontinuous spin glasses. The whole curve depends on the temperature. The saddle point which dominates the partition function, for m constrained replicas, is the point f^* such that the slope of the curve equals m/T (for the usual unreplicated system, $m = 1$). If the temperature is small enough the saddle point sticks to the minimum $f = f_{min}$ and the system is in its glass phase. For $m = 1$, this equilibrium phase transition happens at $T = T_K$.

valley α has a free energy F_α and a free energy density $f_\alpha = F_\alpha/N$. The number of free energy minima with free energy density f is found to be exponentially large:

$$\mathcal{N}(f, T, N) \approx \exp(N\Sigma(f, T)),\tag{4}$$

where the function Σ is called the complexity. The total free energy of the system, Φ, can be well approximated by

$$e^{-\beta N\Phi} \simeq \sum_\alpha e^{-\beta N f_\alpha(T)} = \int_{f_{min}}^{f_{max}} df \exp(N[\Sigma(f, T) - \beta f]),\tag{5}$$

where $\beta = 1/T$. The minima which dominate the sum are those with a free energy density f^* which minimizes the quantity $\Phi(f) = f - T\Sigma(f, T)$. At large enough temperatures the saddle point is at $f > f_{min}(T)$. When one decreases T the saddle point free energy decreases (see Fig. 3, with $m = 1$). The Kauzman temperature T_K is that below which the saddle point sticks to the minimum: $f^* = f_{min}(T)$. It is a genuine phase transition [14–16]. However because $T_c > T_K$, the phase space is actually separated into non-ergodic components (valleys) at $T < T_c$. The total equilibrium free energy is analytic at T_c: in spite of the ergodicity breaking, the system has the same free energy as that of the liquid, as if transitions were allowed between valleys.

What remains of this mean field picture in finite dimensional glasses? When one decreases the temperature, there is a well defined separation of time scales between the α and the β relaxations, which suggests to consider the dynamical evolution of the system in phase space as a superposition of two processes: an intravalley (relatively fast) relaxation, and an intervalley (slow, and getting rapidly much slower when one cools the system) hopping process. One popular way of making this statement more precise, allowing to study it numerically, is through the use of inherent structures

(IS) [37,38]. Given a configuration of the system, characterized by its phase space position $x = \{\vec{x}_1, \ldots, \vec{x}_N\}$, the corresponding inherent structure $s(x)$ is another point of phase space which is the local minimum of the Hamiltonian which is reached from this configuration through a steepest descent dynamics. IS are easily identified numerically [39]. The number of IS at a given energy is often also called the configurational entropy.

Should one identify the IS with the free-energy valleys, and the configurational entropy with the complexity? The answer is no. The difference is very easily seen in spin systems [40]: IS are nothing but configurations which are stable to one spin flip. Zero temperature free energy valleys, defined as TAP states, are stable to the flip of any arbitrarily large number k of spins (but the limit $N \to \infty$ must be taken before the limit $k \to \infty$). In continuous systems, the generalization is clear: IS are local minima of the energy, so that any infinitesimal move of the positions of all N particles raises the energy. Let us generalize the notion of a minimum as follows: define a kth order local minimum as a configuration of particles such that any infinitesimal move of all N particles, together with a move of *arbitrary size* of k particles, raises the energy. The limit $k \to \infty$ gives the definition of a zero temperature 'free' energy valley. The proper definition at finite temperature is known but is slightly more involved [41] and I shall briefly allude to it below, after defining clones. Note that a zero temperature free energy valley cannot be identified by the fact that the Hessian is positive definite: it is necessary that the Hessian be positive in such a state, but this is not a sufficient condition.

The 'entropy crisis scenario' which associates the ideal glass transition with the vanishing of some type of configurational entropy, should thus be taken with a grain of salt in a finite dimensional system. If one considers valleys as IS, and the corresponding configurational entropy, in a system with short range interactions, it is reasonable to expect that one may have two distinct IS which differ by a local rearrangement of a finite number of atoms. It is then easy to show that the slope of configurational entropy versus free energy is infinite around f_{min} [42], which does not agree with the general scenario, except if the Kauzmann temperature vanishes. If one considers valleys as free energy valleys, then two configurations which differ by the (arbitrarily large) displacement of a finite number of atoms are in the same thermodynamic valley. Nucleation arguments then forbid the existence of a non-trivial complexity versus free energy curve in a finite dimensional system: one cannot have excited free energy valleys with an extensive excitation free energy. The solution consists in noticing that there do exist many metastable valleys, with a finite complexity, but these valleys have a finite but very long lifetime (this discussion is very similar to that of the metastability of the supercooled liquid). If this lifetime is much larger than experimental times, the 'mean field' like description neglecting nucleation is a valid approach.

Having somewhat criticized the idea of inherent structure, I would like to point out that the energy landscape is nevertheless a useful tool, not only because it is simpler to describe than the true free energy valleys. Recent studies of the energy landscape in the supercooled liquid phase have shown some evidence that the typical energy E_c of IS found at T_c marks a kind of topological transition between a phase where the nearest saddle of a generic configuration has some unstable directions (above E_c),

and another phase (below E_c) where it is a local minimum [43]. This allows for an interesting conjecture on the difference between fragile and strong glass formers [44]: when the energy decreases through E_c, the dynamics is necessarily activated; if the barriers found at E_c are large compared to kT_c, the system is fragile, otherwise it is strong.

Let us now see briefly how one can go beyond the simple analogy between structural glasses and mean field discontinuous spin glasses. One can actually use the concepts and the techniques which are suggested by this analogy in order to start a systematic first principles study of the glass phase [45–47]. The idea is to postulate the existence of a scenario for the glass transition such as the one found in discontinuous spin glasses, and see how one can use it for computing properties of structural glasses. The validity of such an approach is validated by the predictions it can make. It is not able to prove the existence of a transition. However in physics one often uses very successfully this kind of reasoning, and one should not focus too much on the absence of an existence proof (nobody has proven to you the existence of crystals during your solid state physics course). In fact it could even be that there is no ideal phase transition, the metastable states always have a finite lifetime, but this is so large at low temperatures (around T_K) that the present postulate is a very good starting point (as when one postulates the existence of diamond). A severe limitation at the present stage of development of the theory is that, for technical reasons, we have been able to implement this program only for computing equilibrium properties: we don't know yet how to perform a first principle dynamical computation going in the out of equilibrium regime, below the mode coupling temperature (see however [48]). Instead we shall compute equilibrium properties (typically T_K, the radius of the cage which confine the particles in the glass phase, the configurational entropy etc.) which can be confronted to smart computer simulations on small systems (see e.g. Refs. [49,50]).

The first task is to define an order parameter. This is not trivial in an equilibrium theory where we have no notion of time persistent correlations. The problem is that the glass state seems to have the same symmetry as that of a liquid. However there is a kind of symmetry which is broken in the glass state, and it can be identified by looking at correlations between two replicas of the systems. One introduces two sets of particles which have positions x_i and y_i respectively, the total Hamiltonian is

$$E = \sum_{1 \leqslant i \leqslant j \leqslant N} (v(x_i - x_j) + v(y_i - y_j)) + \varepsilon \sum_{i,j} w(x_i - y_j) \qquad (6)$$

where we have introduced a small attractive potential $w(r)$ between the two systems. The precise shape of w is irrelevant, insofar as we shall be interested in the limit $\varepsilon \to 0$, but its range should be of order or smaller than the typical interparticle distance. The order parameter is then the correlation function between the two systems:

$$g_{xy}(r) = \lim_{\varepsilon \to 0} \lim_{N \to \infty} \frac{1}{\rho N} \sum_{ij} \langle \delta(x_i - y_j - r) \rangle . \qquad (7)$$

In the liquid phase this correlation function is identically equal to one, while it has a non-trivial structure in the glass phase, reminiscent of the pair correlation of a dense liquid, but with an extra peak around $r \simeq 0$. The idea behind this order parameter

is that, if there exist favoured glass structures, they are very difficult to determine a priori, and we don't know how to introduce an external field in order to polarize the system into one of them. However, the second copy, with a weak attraction to the first one, just plays this role of an infinitesimal external field, necessary in order to study a symmetry breaking process (here the symmetry is the global translation of the y particles with respect to the x particles). Let us notice that we expect a discontinuous jump of this order parameter at the transition, in spite of the fact that the transition is of second order in the thermodynamic sense.

Generalizing this approach to a system of m coupled replicas, sometimes named 'clones' in this context (the order parameter used only $m = 2$), provides a wonderful method for studying analytically the thermodynamics of the glass phase [51,52]. In the glass phase, the attraction will force all m systems to fall into the same glass state, so that the partition function is:

$$Z_m = \sum_\alpha e^{-\beta Nm f_\alpha(T)} = \int_{f_{\min}}^{f_{\max}} df \exp(N[\Sigma(f,T) - m\beta f]). \qquad (8)$$

In the limit where $m \to 1$ the corresponding partition function Z_m is dominated by the correct saddle point f^* for $T > T_K$. The interesting regime is when the temperature is $T < T_K$, and the number m is allowed to become smaller than one. The saddle point $f^*(m,T)$ in the expression (8) is the solution of $\partial\Sigma(f,T)/\partial f = m/T$. Because of the convexity of Σ as function of f, the saddle point is at $f > f_{\min}(T)$ when m is small enough, and it sticks at $f^* = f_{\min}(T)$ when m becomes larger than a certain value $m = m^*(T)$, a value which is smaller than one when $T < T_K$ (see Fig. 3). The free energy in the glass phase, $F(m=1,T)$, is equal to $F(m^*(T),T)$. As the free energy is continuous along the transition line $m = m^*(T)$, one can compute $F(m^*(T),T)$ from the region $m \leqslant m^*(T)$, which is a region where the replicated system is in the liquid phase. This is the clue to the explicit computation of the free energy in the glass phase. It may sound a bit strange because one is tempted to think of m as an integer number. However the computation is much clearer if one sees m as a real parameter in (8). As one considers low temperatures $T < T_K$ the m coupled replicas fall into the same glass state and thus they build some molecules of m atoms, each molecule being built from one atom of each 'colour'. Now the interaction strength of one such molecule with another one is basically rescaled by a factor m (this statement becomes exact in the limit of zero temperature where the molecules become point like). If m is small enough this interaction is small and the system of molecules is liquid. When m increases, the molecular fluid freezes into a glass state at the value $m = m^*(T)$. So our method requires to estimate the replicated free energy, $F(m,T) = -\log(Z_m)/(\beta mN)$, in a molecular liquid phase, where the molecules consist of m atoms and m is smaller than one. For $T < T_K$, $F(m,T)$ is maximum at the value of $m = m^*$ smaller than one, while for $T > T_K$ the maximum is reached at a value m^* larger than one. The knowledge of F_m as a function of m allows to reconstruct the configurational entropy function $Sc(f)$ at a given temperature T through a Legendre transform. The Kauzmann temperature ('ideal glass temperature') is the one such that $m^*(T_K) = 1$. For $T < T_K$ the equilibrium configurational entropy vanishes. This gives the main idea which allows to compute the free energy in the glass phase, at a temperature $T < T_K$, from first principles: it is equal

to the free energy of a molecular liquid at the same temperature, where each molecule is built of m atoms, and an appropriate analytic continuation to $m = m^*(T) < 1$ has been taken. The whole problem is reduced to a computation in a liquid. This is not trivial, and requires to develop some specific approximations. I shall not elaborate on that here, but refer the reader to the original papers [46,53–55]. Let me just mention one point which one should keep in mind: so far this analytic approach involves some low temperature expansion, where the possibility for two molecules to exchange atoms is not taken into account. Within this approximation the difference between pure states and IS is not seen. The results are in good agreement with numerical simulations on various systems like binary soft spheres or binary Lennard-Jones; a good test is the computation of the configurational entropy. One should also notice that recent numerical simulations on small systems point towards the possible existence of an equilibrium phase transition at a temperature T_K close to that predicted by this theory [50] (to be precise the theory assumes the existence of this ideal glass transition, and can then compute the value of T_K).

The existence of metastable states in the temperature range T_K, $T < T_c$ can be confirmed by studying the potential $W(q)$ which is the Legendre transform of the free energy $F(\varepsilon)$ for one replica (particles y) coupled as in (6) to a reference equilibrated system (particles x)

$$W(q) = F(\varepsilon) + \varepsilon q, \quad q = \frac{-\partial F}{\partial \varepsilon} . \tag{9}$$

Analytic computation in mean field models [41], as well as in glass forming liquids using the replicated HNC approximation [56], show that $W(q)$ is minimal at $q = 0$, but has a secondary minimum at a certain $q = q_{EA}$, in the temperature range $T_K < T < T_c$. The behaviour around this second, metastable, minimum corresponds to phenomena that can be observed on time scales shorter than the lifetime of the metastable state (this lifetime is infinite in the mean field models, but becomes finite in a real system because of nucleation effects).

Let us summarize the present situation in a few words. There is a far reaching analogy between structural glasses and the theoretical mean field models of discontinuous spin glasses. Inspired by this analogy, some of the powerful methods and concepts used in spin glass theory have been applied to standard simple models of glass formers like binary Lennard Jones systems. These allow to perform some first principle computations of the equilibrium properties of these systems. I think that some real progress has been made, but the hardest part is still ahead of us: we now need to understand the nucleation properties in order to be able to determine the lifetime of metastable states and to compute the fast increase of the relaxation time in the regime between T_c and T_K. The out of equilibrium dynamics also contains many open problems. The aging behaviour can be found within several different theoretical approaches, but these in fact relate to rather different physical mechanisms. It seems to me rather plausible that a glass, when cooled, will evolve through different aging regimes, starting with a regime (well described by the mean field dynamics) where it seeks unstable directions in the energy landscape, and evolving to a 'trap-like' regime at longer times. More work, theoretical and experimental is needed in order to disentangle these various regimes.

My belief is that a careful study of some recently introduced lattice models [57] could offer the best route to answering all these questions.

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