Calorimetric glass transition in a mean-field theory approach

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The study of the properties of glass-forming liquids is difficult for many reasons. Analytic solutions of mean-field models are usually available only for systems embedded in a space with an unphysically high number of spatial dimensions; on the experimental and numerical side, the study of the properties of metastable glassy states requires thermalizing the system in the supercooled liquid phase, where the thermalization time may be extremely large. We consider here a hard-sphere mean-field model that is solvable in any number of spatial dimensions; moreover, we easily obtain thermalized configurations even in the glass phase. We study the 3D version of this model and we perform Monte Carlo simulations that mimic heating and cooling experiments performed on ultra-stable glasses. The numerical findings are in good agreement with the analytical results and qualitatively capture the features of ultra-stable glasses observed in experiments.

To test this scenario, it would be necessary to perform experiments and simulations at various temperatures in this range, but then one must face the problem of equilibrating the glass former at temperatures $T \approx T_K < T_g$ (where $T_g$ is the phenomenological glass transition temperature), where it is by definition impossible to do so. Indeed, a simple estimate shows that the increase of the equilibration time below $T_d$ is so sharp that one cannot get nearer to $T_K$ than $\Delta T \approx \frac{1}{2} T_K$ without falling out of equilibrium, making it impossible for us to get a good look at the lowest states: Only the high free-energy states near $T_g$ can be probed experimentally.

Some progress in this direction has been made recently both in experiments (9) and numerical simulations (10), with the introduction of the so-called vapor deposition technique, which allows one to obtain extraordinarily stable glasses [usually referred to as ultra-stable glasses (10–13)] in a relatively short time, even for temperatures much lower than $T_d$. First numerical simulations on an ultra-stable glass of binary Lennard-Jones mixture seem to support the existence of a thermodynamic phase transition (10). On the theoretical side, the intrinsic out-of-equilibrium nature of glass poses another challenge, because the methods of equilibrium statistical mechanics cannot be used in the usual way, requiring, in principle, to resort to dynamical tools. This strategy is actually viable and was used, for example, by Keys et al. (14), where a suitably tuned East model has been shown to reproduce well the experimental behavior observed in DSC (differential scanning calorimetry) experiments on different glass-former materials, for example glycerol (15) and boron oxide (16). This approach, however, has the drawback of being phenomenological in nature.

The recent introduction (17) of a semirealistic soluble model for glasses, the Mari–Kurchan (MK) model, gives us the possibility of addressing both the equilibration and the theoretical problem. It allows us to obtain equilibrated configurations also

Significance

Understanding the properties of glasses is one of the major open challenges of theoretical physics. Making analytical predictions is usually very difficult for the known glassy models. Moreover, in experiments and numerical simulations thermalization of glasses cannot be achieved without sophisticated procedures, such as the vapor deposition technique. In this work we study a glassy model that is simple enough to be analytically solved and that can be thermalized in the glassy phase with a simple numerical method, opening the door to an intensive comparison between replica theory predictions and numerical outcomes.

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beyond the dynamical transition and deep into the glass phase, using the so-called planting method (18). Moreover, it is in principle solvable in the replica method, allowing us to study the metastable glassy states with a static formalism, without having to solve the dynamics.

Our aim is to use this model to simulate slow annealing experiments usually performed on glasses and ultrastable glasses, to compare the numerical outcomes with experimental results and theoretical predictions in the replica method.

The Model
We consider the potential energy of the family of models introduced by Mari and Kurchan (MK model) (17):

\[ V(\mathbf{x}, l) = \sum_{\{ij\}} v(x_i - x_j - l_k), \]

where \( \mathbf{x} = \{x_1, \ldots, x_N\} \) are \( N \) \( d \)-dimensional vectors, representing particles positions, and the particles move in a \( d \) dimensional cube of size \( L \), with periodic boundary conditions. The main feature of the model is the variables \( l = \{l_k\} \): They are \( N(N - 1)/2 \) quenched random vectors, called random shifts, independently drawn out from a uniform probability distribution inside the cube. The function \( v \) could be in principle any interesting short-range repulsive pair-wise interaction.

The main effect of the random shifts is to destroy the direct correlation among the particles that interact with a given particle (17). This makes the computation of static quantities very simple, because in the Mayer expansion of the grand-canonical potential only the tree diagrams survive in the thermodynamic limit (17). The idea is quite old (19), and had important applications to turbulence, but has only been recently applied to glasses.

Static Thermodynamic Properties in Liquid Phase. Here we will summarize analytical and numerical results obtained by Mari and Kurcan for this model. In the following \( D \) will denote the diameter of spheres. In hard-sphere systems the potential \( v(\mathbf{x}) \) is infinite at distances less than \( D \) and the role of inverse temperature is played by the packing fraction \( \rho = N\nu_d(D)/L^d = \rho\nu_d(D) \), where \( \nu_d(D) \) is the volume of the \( d \)-dimensional sphere of diameter \( D \); we will call it density absorbing the multiplicative factor in its definition.

The Hamiltonian contains random terms and the interesting quantities have then to be averaged over these parameters. We can define the annealed entropy \( S^A \) and the quenched entropy \( S^Q \) given by

\[ S^A \equiv \log \left( \frac{Z(\mathbf{l})}{Z} \right), \quad S^Q \equiv \log (Z). \]

The computation of \( S^A \) can be easily done and one finds

\[ S^A(\rho) = \frac{S^A(\rho)}{N} = -\log(\rho) - 2^{d-1} \nu_d(D) \rho + \log(N). \]

The presence of the \( \log(N) \) term is due to the fact that in this model particles are distinguishable for a given realization of random shifts.

A more interesting quantity is the quenched entropy. In this model one finds that \( S^Q(\rho) = S^Q(\rho) \) in the liquid phase (i.e., below the Kauzmann transition density \( q_{\text{K}} \)). The Kauzmann transition is avoided in the thermodynamic limit: The total entropy \( S^Q \) grows as \( \log(N) \) whereas the vibrational entropy is a non-decreasing function of \( \rho \) that diverges in the infinite-density limit. This implies that the configurational entropy contains a term proportional to \( \log(N) \). As a consequence, the Kauzmann density \( q_{\text{K}} \) (i.e., the point where the configurational entropy vanishes) diverges logarithmically in the thermodynamic limit.

Using standard thermodynamic relations one can derive from Eq. 3 the liquid-phase equilibrium equation of state

\[ P = \rho + 2^{d-1} \nu_d(D) \rho^2, \]

where \( P \) is the pressure.

For what concerns the radial distribution function, one has to take the random shifts into account:

\[ g(r) = \frac{1}{\rho^2} \sum_{\{ij\}} \delta(|x_i - x_j + l_k| - r), \]

where the bracket average is computed using the ensemble distribution function (Gibbs-Boltzmann distribution at equilibrium) and the bar average is computed using the random shifts probability distribution. The result is

\[ g(r) = \theta(r - D), \]

where \( \theta \) is the usual Heaviside step function. This result is the same obtained with high-dimensional hard spheres (20), but the mean-field nature of the model has allowed us to get it in any number of spatial dimensions. The equilibrium pressure is related to density by the usual relation for hard spheres (21),

\[ P = \rho + 2^{d-1} \nu_d(D) g(r) \rho^2, \]

from which, using Eq. 6, the equilibrium equation of state (Eq. 4) can be derived again.

Glassy Properties. The model is interesting because despite the extreme simplicity of the statics (a feature that it has in common with facilitated models) the dynamics is extremely complex. At high densities there is the glass phase that in the thermodynamic limit is separated from the liquid phase by a mode coupling transition. This transition exists only if we embed the model in a space with an infinite number of dimensions \( d \); when \( d < \infty \), hopping effects destroy the transition, which becomes only a cross-over region (22).

Accurate simulations (22) give a higher value for the mode-coupling dynamical density (i.e., \( q_{\text{MC}} = 1.91 \)). A more careful analysis of the properties of the system near the putative mode-coupling transition can be found in ref. 22, where the effects of hopping are carefully studied. Other features, such as a violation of the Stokes–Einstein relation and dynamical heterogeneities, are present in this model (17, 22).

Numerical Simulations
When a glass is gradually heated during DSC experiments thermodynamic quantities, like the internal energy, continue to follow the glassy behavior also in the liquid phase, until the so-called onset temperature \( T_{\text{on}} \) is reached. For \( T > T_{\text{on}} \) the system gradually approaches equilibrium; during this relaxation process the specific heat reaches a maximum value, higher than the equilibrium one. The value of \( T_{\text{on}} \) quantifies the stability of the initial glass and is considerably higher for glasses prepared through the vapor deposition technique than ordinary glasses aged for many months (9, 10). The vapor deposition procedure has been recently mimicked by a computer algorithm, and numerical simulations over a Lennard-Jones binary mixture showed the same behavior (10, 11).

We aim to study numerically this deviation from equilibrium in the liquid region and the subsequent relaxation process in the MK model. In the MK model we are able to obtain equilibrium configurations beyond the dynamic transition via a special procedure, allowed only by the presence of random shifts, the
so-called planting (18) method. Basically, planting consists of two steps: the generation of a random configuration of sphere positions, independently drawn out from the uniform distribution over the volume, and the generation of the random shifts \( \{ l_i \} \) so that the nonoverlap condition imposed by the hard-sphere potential energy (Eq. 1) is satisfied for every pair of spheres (see Supporting Information for details). The mean-field nature of the interaction guarantees that planted configurations are equilibrated (18). The planted glass in the MK model, like vapor-deposited ultrastable glasses in real world, is the best possible starting point for the study of the deviation from equilibrium in the liquid phase. We start from a planted configuration and mimic DSC heating experiments by running adiabatic stepwise decompression scans, where the system performs jumps between different density values and a large number of Monte Carlo steps for each density value, to reach thermalization.

We refer to Supporting Information for all other simulation details. We present now the results of numerical simulations, based on the Monte Carlo method, of a system composed of \( N = 800 \) spheres of diameter \( D = 1 \) in \( d = 3 \) dimensions, with periodic boundary conditions.

**Decompression Jump and Spheres Contact Region Emptying.** The outcome of the planting technique is a thermalized initial configuration at a certain density \( \varphi_0 > \varphi_d \) (see Fig. S1). We discuss now the effects a density jump \( \varphi_0 \rightarrow \varphi_1 \) on \( g(r) \), where \( \varphi_1 < \varphi_0 \) (decompression). Results for \( \varphi_0 = 2.5 \) and \( \varphi_1 = 1.7 \) are shown in Fig. 1. When the sphere radius is decreased, particles originally in contact separate, causing a drop of the liquid region and for densities sufficiently far from the dynamical transition it is possible to see a complete filling. In the liquid region and for densities sufficiently far from the dynamical transition it is possible to see a full filling.

We consider now the following decompression protocol: We start from a planted configuration at \( \varphi_0 = 2.5 \), we jump to \( \varphi_1 = 1.6 \) and wait \( 2^{22} \) steps, then we jump to \( \varphi_2 = 1.55 \) and we wait again \( 2^{22} \) steps, then \( \varphi_3 = 1.5 \) and \( \varphi_4 = 1.45 \). Fig. 2 shows the temporal behavior of \( g(1) \) for various values of \( \varphi \). We do not see structural relaxation for \( \varphi = 1.55, 1.5 \) (liquid phase): the system, after a partial, fast relaxation process reaches the metastable plateau and it does not have enough time to escape. When \( \varphi = 1.45 \), the lifetime of the original metastable state is smaller than \( 2^{22} \) steps and we observe a clear structural relaxation, corresponding to the complete filling of the contact zone.

**Mean Square Displacement and Structural Relaxation Time.** To study the behavior of the relaxation time as a function of density in the liquid phase and evaluate the dynamic glass transition density \( \varphi_d \), we turn our attention to another observable, the mean square displacement \( \Delta(t) \) (MSD) of spheres from their initial positions:

\[
\Delta(t) = \frac{1}{N} \sum_{i=1}^{N} |x_i(t) - x_i(0)|^2.
\]

Because we are interested only in the relaxation time, we start from a thermalized configuration at \( \varphi_0 = 2.5 \) and we jump directly to the density value \( \varphi \) we are studying. We stress that in Eq. 8 \( x_i(0) \) is physical position of sphere \( i \) immediately after the density jump. We let the system evolve for \( 2^5 \) steps at this density \( \varphi \). For \( \varphi < \varphi_d \), as expected in a glassy system not too far from its dynamical glass transition, we can observe a two-step relaxation process: the system reaches a metastable plateau after about \( 2^{10} - 2^{11} \) steps, remains trapped in it for a long time, after which structural relaxation occurs. For each value of density we fitted the MSD's escape from the plateau with a power law function and obtained the value of the relaxation time (see Supporting Information for details). We fitted the resulting curve of \( \tau_0 \) as a function of \( \varphi \), displayed in Fig. 3, with the power law behavior \( \tau_0 = A(\varphi_0 - \varphi)^{-\gamma} \), obtaining in this way \( \varphi_0 = 1.73 \pm 0.04, \gamma = 4.1 \pm 0.7 \). One can notice that the value for \( \gamma \) is not too different from the one obtained in ref. 17 performing a similar analysis on the relaxation time, whereas the value of \( \varphi_0 \) is definitely smaller than \( \varphi_d \), but not too far from the one obtained in ref. 17.

**Decompression and Compression Scans: Qualitative Comparison with Experiments.** In Fig. 4 we represent the behavior of the reduced pressure \( P/P_0 \) as a function of density for a decompression protocol with starting density \( \varphi_0 = 2.5 \) and a constant density-jump amplitude \( \Delta \varphi = \varphi_n - \varphi_{n-1} = \varphi_1 - \varphi_0 \). We have different curves for
This deviation continues for the largest density values below stable state and pressure deviates from its equilibrium value in the glass phase, so relaxation takes place inside the original metastable state, not yet having sufficient time to reach equilibrium. When density is sufficiently low, the lifetime of the original metastable state becomes smaller than \(2^k\) and the onset of relaxation toward equilibrium takes place. The relatively sharp pressure reclimb is dependent on decompression rate, and it is faster for slower rates.

The decompression protocol adopted for our system, composed by hard spheres, is equivalent to the typical DSC’s heating scans, with two crucial differences. (i) In DSC experiments we move toward the glassy phase by decreasing the temperature: In the case of hard spheres the inverse of the density plays the same role of the temperature. (ii) The starting configurations of the dynamics are fully equilibrated and this corresponds only to the case of DSC with infinitely slow cooling speed and relatively fast heating speed. The observed deviation of pressure from equilibrium for \(\varphi > \varphi_d\), for example \(\varphi = 1.6, 1.65, 1.7\): The system continues to relax inside the original metastable state, not yet having sufficient time to reach equilibrium. When density is sufficiently low, the lifetime of the original metastable state becomes smaller than \(2^k\) and the onset of relaxation toward equilibrium takes place. The relatively sharp pressure reclimb is dependent on decompression rate, and it is faster for slower rates.

Fig. 3. Relaxation time as a function of density, computed as described in the text. Red points are the result of an extrapolation (when \(kR\) is larger than the largest number of performed Monte Carlo steps at each density value, i.e., \(2^k\) steps) so they were discarded in the fit. Blue line is the fit result.

Replica Computation of Metastable States Curves

So far we have shown how the MK model allows one to prepare the system in a glass state, even at densities much higher that the dynamical one, without incurring the problem of extremely large equilibration times. In addition, this model has another remarkable advantage: It is in principle solvable, thanks to its mean-field nature. The interaction network is tree-like (or, alternatively, without loops) in the thermodynamic limit, like in Van der Waals liquids (17, 21), and thus it also allows for a ready comparison between numerics and analytic computations. In particular, it allows us to perform computations in the replica method. Although the MK model is soluble, its actual analytic solution is exceedingly complex (23), so we have to resort to some kind of approximation: Here we assume that the cages have a Gaussian shape (22).

In the replica approach to the glass transition (1, 4), it is assumed that for densities \(\varphi > \varphi_c\) the configuration space can be unambiguously split in subsets, denoted as metastable glassy states. These states are theoretically identified with the local minima of a suitable functional, which plays in this context the same role of the Thouless–Anderson–Palmer free energy in spin glasses (2).

In a mean-field situation and in the thermodynamic limit, where metastable states live forever, the system becomes then immediately trapped in one of these states and fails permanently to attain relaxation (the so-called mode coupling transition). However, out of mean field or with finite system size the system will be finally able to hop out of the state (22) and relax, although an extremely long time will be needed to do so (5).

The most important feature of these metastable states is that they are degenerate, that is, they can have the same free entropy. In fact, if one fixes a density \(\varphi > \varphi_c\) and a value \(s\) for the free entropy, it is possible to see that the number of states that share it (in the functional picture, the number of minima that all have the same height \(s\)) scales exponentially with the size of the system, \(N(s, \varphi) \propto e^{s(s, \varphi)}\). This causes the total free entropy of the system to gain an extra term to take this fact into account:

\[
S(s, \varphi) = s + \Sigma(s, \varphi),
\]

where \(\Sigma(s, \varphi)\) is called complexity (or, alternatively, configurational entropy), a central quantity in replica theory.

Fig. 4. Reduced pressure \(p\) as a function of density in a decompression protocol with \(\varphi_0 = 2.5, \Delta \varphi = 0.05\). Different colors correspond to different decompression rates (\(k\) is the number of Monte Carlo steps performed at each density value).
The replica method provides us with a standard procedure to compute the complexity and also the in-state entropy (24). Its concrete application to hard-sphere systems is described in full detail in section III of ref. 4; here we recall it briefly. It consists of introducing $m$ independent replicas of the system and forcing them to occupy the same metastable state. The entropy of the replicated system becomes then

$$S(m, \varphi) = \Sigma(\varphi, s) + ms(\varphi),$$

where $s$ is the free entropy of the state. In the thermodynamic limit, the partition function will be dominated with probability 1 only by the states with the entropy $s_{\text{eq}}$ that satisfies the optimum condition

$$\frac{d\Sigma(s, \varphi)}{ds} + m = 0. \tag{9}$$

The in-state entropy $s_{\text{eq}}(m, \varphi)$ of those states and their complexity $\Sigma_{\text{eq}}(m, \varphi)$ can then be derived using the following relations:

$$s_{\text{eq}}(m, \varphi) = \frac{dS(m, \varphi)}{dm} \tag{10}$$

$$\Sigma_{\text{eq}}(m, \varphi) = m^2 \frac{\partial^2[m^{-1}S(m, \varphi)]}{\partial m^2} \tag{11}$$

and the function $\Sigma(s, \varphi)$ can then be reconstructed from the parametric plots of $s_{\text{eq}}(m, \varphi)$ and $\Sigma(m, \varphi)$.

Isocomplexity Approximation. The replica formalism has been applied to the study of infinite dimensional hard spheres in a series of papers (20, 25, 26) with remarkable success. However, those results concern only the properties of the glass former after equilibration, whereas our numerical results concern the glass former when it is still trapped inside a metastable state, before equilibration takes place. Indeed, one could argue that for experimental and practical purposes, getting predictions for this regime is even more important than the study of the equilibrium solution for infinite waiting times. This program, however, poses a challenge because in principle it requires solving the dynamics for different preparation protocols. To this day, the only first-principles dynamical theory for glass formers is the mode coupling theory (8), which performs well near the dynamical transition but notoriously fails at higher densities, forcing one to use phenomenological models for the description of the high-density (or low-temperature) regime, as done by Keys et al. (14). We present here a computation that has the advantage of being both fairly simple and static in nature.

Because the system is trapped in a single metastable state during the simulation, it is clear that its physical properties are determined only by the in-state entropy $s(\varphi)$ of that single state. We can easily determine $s_{\text{eq}}$ at the beginning of the experiment, when the system is at equilibrium and it corresponds to $s_{\text{eq}}(\varphi_0, 1)$, but it is nontrivial to determine it when the density is changed and the system falls out of equilibrium, because Eq. 9 allows us to compute only quantities related to the states that dominate the partition function. Indeed, we can see that for every density $\varphi$ we can choose the value of $s_{\text{eq}}$ simply by appropriately tuning the parameter $m$, but in principle we still have no way of knowing what is actually the state the system is trapped into, that is, we lack a criterion to choose a function $m(\varphi)$ consistent with the requirement that the system remain trapped in a single metastable state (27).

To overcome this difficulty, we assume that every state can be followed in density without any crossings between states, or bifurcations, or spinodal points (28); this means that the number (and thus the complexity) of states that share the same value $s$ of the in-state entropy is a conserved quantity during the experiment and can then be used as a label for the states. This method is usually referred to as isocomplexity (27, 28).

In summary, to choose $m(\varphi)$ we impose that

$$\Sigma(m(\varphi), \varphi) = \Sigma(1, \varphi_0) = \Sigma_0 = \text{const}. \tag{12}$$

This assumption is false in most cases. For example, it has been recently shown that for infinite-dimensional hard spheres a full replica symmetry breaking scenario holds for sufficiently high density (26), invalidating the isocomplexity hypothesis. The only exact method to tackle the problem would then be the state-following approach, which uses the two-replica potential as a central tool (3). However, this method is far more complex and its application goes beyond the scope of this paper; here we always use the isocomplexity approximation, referring to ref. 29 for the complete state-following computation. For a systematic comparison of the different approaches in the context of $p$-spin glasses, see ref. 30.

We refer to Supporting Information for details of the computation of the isocomplexity lines displayed in Fig. 6. Once the potential $s_{\text{eq}}^2(\varphi) = s_{\text{eq}}(m_{\Sigma}(\varphi), \varphi)$ has been obtained, one can compute

![Graph](image-url)
the desired physical observables using standard thermodynamic relations (21). Final results for pressure during decompression and compression are shown in Fig. 5 and compared with simulation results. There is a good agreement between analytical and numerical curves, especially for density values not too far from \( \varphi_0 \).

**Conclusions**

We studied a mean-field model of glass transition, the MK model. We were able both to obtain a stable glass, thanks to the planting technique, and to study numerically and analytically (within replica method and isocomplexity assumption) the variations of pressure caused by relatively fast changes of density. We showed, both numerically and analytically, that qualitatively this model displays the same behavior of experimental ultrastable glasses reported in refs. 9 and 10. Our model seems to show a first-order phase transition when evading from metastable equilibrium (see ref. 29 and Supporting Information). This is in qualitative agreement with experiments, which show a first-order phase transition when evading from metastable equilibrium.

We have also shown that the RFOT approach, together with the replica method, is able to qualitatively describe the process of glass formation through a slow annealing, with very little computational cost and without resorting to a posteriori phenomenological considerations. Our results can be compared with the DSC experiments where cooling is much slower than heating and as a result the cooled configurations (before heating) may be approximated with equilibrium configurations. We can study this situation in the MK model just because we can plant a thermalized equilibrium configuration at the density we prefer. The very interesting problem of understanding the behavior of DSC experiments when the cooling speed is the same (or faster) than the heating speed is not studied in this paper: In this situation analytic computations could be done only if we had the dynamics under analytic control, a goal that has not yet been reached.

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**Supporting Information**

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**Simulation Details**

**Planting Method.** We generate the initial configuration as follows:

- We generate randomly the positions $x$ of the $N$ spheres, with a uniform probability distribution over the simulation box.
- For each sphere $i$, we generate its shifts $l_i$ with uniform distribution in the simulation box. Each shift $l_i$ is accepted if and only if

$$|x_i - x_j + l_i| > 1,$$  \[\text{[S1]}\]

otherwise it is generated again until condition **S1** is satisfied.

It can be shown (1) that in the infinite volume limit this procedure generates a thermalized initial configuration where the annealed average of entropy is equal to the quenched one (i.e., a configuration in the liquid phase) (1).

We have tested that the procedure works, that the configurations that we generate are at equilibrium and their properties are independent from time (as long as the density remains constant). The result for the observable $g(r,0)$ for planting density $\varphi_0=2.5$ is shown in Fig. S1. We can see in the low $r$ region a behavior compatible with the equilibrium one:

$$g(x-y) = \exp(-v(x-y)) = \begin{cases} 0 & \text{if } |x-y| < D \\ 1 & \text{if } |x-y| > D \end{cases}$$  \[\text{[S2]}\]

within 1 or 2 SDs. For example, for the contact point we have $g(1)=0.987 \pm 0.019$. We do not study the large $r$ behavior of $g(r,0)$, which shows a decay caused by the finite size of the simulation box and cannot be compared with the infinite-volume analytical result (Eq. S2).

**Monte Carlo Evolution Algorithm and Verlet Lists.** We used a Monte Carlo evolution algorithm. At each step $t$ we propose a displacement $\Delta x_i(t)$ to each sphere $i$. The proposed displacement is generated uniformly in a 3D sphere of radius $\delta$, where $\delta = 0.2$ is a fixed parameter. The proposed displacement is accepted if and only if the condition

$$|x_i + \Delta x_i - x_j + l_i| > 1$$  \[\text{[S3]}\]

is satisfied for all other spheres $j \neq i$; otherwise it is rejected. This stochastic dynamics satisfies the detailed balance property, thus implying relaxation toward equilibrium. To reduce computational time we use Verlet lists (see, e.g., ref. 2).

**Radial Distribution Function Computation.** We denote by $\Omega_{\Delta_{x}}(r,t)$ the number of sphere couples such that

$$|x_i(t) - x_j(t) + l_i| \in [r, r+\Delta]$$

and we define a fixed time radial distribution function

$$g_{\Delta}(r,t) = \frac{1}{4N\varphi} \frac{\Omega_{\Delta_{x}}(r,t)}{(r+\Delta)^3}$$

The parameter $\Delta$ is fixed and corresponds to the histogram bin length. We choose $\Delta = 0.05$. To gain central processing unit time we perform measurements at equispaced intervals in time (typically every 20 Monte Carlo sweeps). In our simulation we further average over the different starting configuration. The number of configurations is $M=6$, a reasonable value for a self-averaging quantity. The statistical error is estimated from sample-to-sample fluctuations.

**Decompression Protocol.** In the following we denote by $k$ the logarithm in base 2 of the number of Monte Carlo steps performed for each density value. We are interested in a decompression protocol that mimics the physical heating of a glass. We start from a planted initial configuration at a density $\varphi_0$ in the glassy region ($\varphi_0 > \varphi_c$) in the liquid phase ($\varphi_0 < \varphi_0$), equivalent to the supercooled liquid region in real glass formers. To be safe we choose $\varphi_0$ values between 2 and 3. After planting, we decompress the system changing the box size, leaving the integer positions unchanged, causing a jump $\varphi_0 \rightarrow \varphi_1$ of density, with $\varphi_1 < \varphi_0$. The system evolves for $2^k$ Monte Carlo steps at density $\varphi_1$, then density jumps again to a lower value $\varphi_2 < \varphi_1$, the system evolves for $2^k$ steps at density $\varphi_2$, and so on.

**Compression Protocol.** To compress the system, we increase the particle radius until the particles touch. When this happens, Monte Carlo steps are performed to separate the particles; afterward, the radius is increased again, until the final density is reached.

The procedure is slow and therefore the final system is nearly thermalized. After the final density is reached, we run a long simulation for final thermalization and we take measurements only in the second half of the run.

**Mean Square Displacement**

For each density value $\varphi$ we measured the relaxation time by fitting the plateau escape region of the MSD $\Delta(t)$ with the power law

$$\Delta(t) = a(1 + ct^b).$$

We discarded the fast relaxation region. We considered for each density value only points with $t > 2^{11}$. We defined the relaxation time using the relation $\Delta(t_R) = 1.5 \Delta(2^{11})$. The value 1.5 is somewhat arbitrary: It should be neither too small, to reduce noise effects, nor too large, to allow us to obtain relaxation time values not too large compared with the typical time scales of our simulations. Using this procedure we obtained the value of relaxation time for each value of density. For the highest studied values of density (i.e., $\varphi = 1.7, 1.68, 1.66$), we obtained $\tau_R > 2^{22}$, meaning that $2^{22}$ steps were not sufficient to observe relaxation: These are extrapolated points and we discarded them.

**Computation of Isocomplexity Lines**

The first step is the computation of the replicated entropy $S(m, \varphi)$ as a functional of the replicated density. Denoting by $\mathbf{X} = \{\mathbf{x}^{(i)}\}$ the set of the positions of the $m$ replicas, by $\rho(\mathbf{x})$ the replicated density, for the mean-field MK model we have

$$S(m, \varphi) = - \int d\mathbf{x} \rho(\mathbf{x}) \log(\rho(\mathbf{x}))$$  \[\text{[S4]}\]

$$+ \frac{1}{2} \int d\mathbf{x} \int d\mathbf{y} \rho(\mathbf{x})\rho(\mathbf{y}) f(\mathbf{x} - \mathbf{y}) + N \log(N),$$

where

$$f(\mathbf{x} - \mathbf{y}) = \exp \left( \sum_{n=1}^{m} v(\mathbf{x}^{(n)} - \mathbf{y}^{(n)}) + 1 \right) - 1$$

Mariani et al. www.pnas.org/cgi/content/short/1500125112 1 of 3
is the replicated Mayer function. In practice, the replicated density is usually parameterized as
\[
\rho(x) = \frac{N}{V} \int dx \prod_{a=1}^{m} g_{a}(x^{a} - X),
\]
where \(x^{a}\) is the position of replica \(a\) and \(g_{a}\) is the Gaussian function with variance \(A\). The parameter \(A\) represents the average cage radius and can be also interpreted as the plateau value of the mean square displacement of particles in the caging regime. For the mean-field MK model of hard spheres, combining results presented in appendix A of ref. 3 and in section VI of ref. 4, putting parameterization S5 in S4 we obtain
\[
S(m, \varphi, A) = \log(N) - \log \left( \frac{\varphi}{V \rho(1)} \right) + S_{\text{harm}}(m, A) - 2^{d-1} \varphi(1 - G(m, A)),
\]
where \(G(m, A)\) and \(S_{\text{harm}}(m, A)\) are defined in ref. 4. We stress that Eq. S6 is the same of a pure hard-sphere system (that is, without shifts) in infinite dimension. We must then optimize this with respect to \(A(4)\), getting the equation
\[
\frac{1}{\varphi} = F(m, A(m, \varphi)),
\]
where \(\varphi = 2^{d} \varphi/d\) and
\[
F(m, A) = A \frac{\partial G(m, A)}{\partial A}.
\]
Eq. S16 and the form of the function \(F(4)\) imply a first-order transition at the endpoint of metastable curves, both in the \((m, \varphi)\) plane and in the pressure-density plane. We discuss this result in Singularity of Cage Radius and Pressure at the Clustering Line.

We plug the solution \(A(m, \varphi)\) of Eq. S16 in Eq. S6, obtaining \(S(m, \varphi)\). Using then the replica relations
\[
s_{\text{eq}}(m, \varphi) = \frac{\partial S(m, \varphi)}{\partial m},
\]
\[
\Sigma_{\text{eq}}(m, \varphi) = m^{2} \frac{\partial [m^{-1} S(m, \varphi)]}{\partial m},
\]
on Eq. S6 we get the following expression for the complexity:
\[
\Sigma(m, \varphi, A) = S(m, \varphi, A) - \frac{1}{2} (1 + m + m \log(2\pi)) + 2^{d-1} \varphi H(m, A),
\]
where
\[
H(m, A) = -m \frac{\partial G(m, A)}{\partial m}.
\]
The only remaining task is now to solve the equation
\[
\Sigma(m, \varphi) = \Sigma_{0} = \Sigma(1, \varphi_{0})
\]
with respect to \(m\), for various values of \(\varphi\). Because in the clustering region \(\Sigma\) is a decreasing function of \(m\) at fixed \(\varphi\), the solution \(m_{\Sigma_{0}}(\varphi)\) of the isocomplexity condition can be found with a simple bisection algorithm. We start at \(\varphi_{0}\), then we change the density of a small amount \(\Delta \varphi\), and we use bisection to find the solution \(m_{\Sigma_{0}}\) of the equation
\[
\Sigma(m, \varphi_{0} + \Delta \varphi) = \Sigma_{0}.
\]

Once it has been found, we change the density again and the procedure is repeated until the clustering line is reached and the solution for \(A\) disappears.

In-State Pressure
In principle the ratio \(p(\varphi)\) between physical pressure \(P(\varphi)\) of a state of complexity \(\Sigma_{0}\) and density \(\varphi\) can be computed using the relation
\[
p(\varphi) = \rho^{-1} P(\varphi) = -\varphi \frac{d}{d \varphi} s_{\text{eq}}(m(\varphi), \varphi),
\]
where \(m(\varphi)\) solves Eq. S12 for a given complexity value \(\Sigma_{0}\). Eq. S13 is uncomfortable because it involves also the partial derivative with respect to \(m\). Instead of directly using Eq. S13 we define a modified replicated entropy for each complexity value \(\Sigma_{0}\):
\[
\tilde{S}(m, \varphi) = S(m, \varphi) - \Sigma_{0} = m s_{\text{eq}}(m, \varphi) + \Sigma_{\text{eq}}(m, \varphi) - \Sigma_{0}.
\]
Isocomplexity Eq. S12 is then equivalent to the equation
\[
m^{2} \frac{\partial}{\partial m} \left[ m^{-1} \tilde{S}(m, \varphi) \right] = 0.
\]
Therefore, the pressure of a metastable state can be expressed in terms of total entropy \(\tilde{S}\):
\[
p(\varphi) = - \frac{\varphi}{m(\varphi)} \frac{\partial}{\partial \varphi} \left( \tilde{S}(m, \varphi) \right)_{m=m(\varphi)} = - \frac{\varphi}{m(\varphi)} \frac{\partial}{\partial \varphi} \left( S(m, \varphi) \right)_{m=m(\varphi)}.
\]
Eq. S15 is all we need to pass from \((m, \varphi)\) plane to the pressure-density plane. It is also easy to pass to the contact value of radial distribution function through the relation \((5) g(1) = (p - 1)/(4 \varphi)\).

Singularity of Cage Radius and Pressure at the Clustering Line
For each metastable curve \(m(\varphi)\) the clustering point \(\varphi_{d}\) is defined as the lowest \(\varphi\) value for which equation
\[
\frac{1}{\varphi} = F(m, A(m, \varphi))
\]
admits a finite solution \(A(m(\varphi), \varphi)\). The corresponding cage radius \(A_{\text{max}}\) is the value of \(A\) for which \(F(m(\varphi_{d}), A)\) has a maximum \((4)\). Expanding \(F(m, A)\) in Taylor power series near \(\varphi_{d}\) and rearranging terms we obtain from Eq. S16
\[
A(\varphi) - A_{\text{max}} = C \sqrt{\varphi - \varphi_{d}} + O(\varphi - \varphi_{d}),
\]
where \(A_{\text{max}} = A(m(\varphi_{d}), \varphi_{d})\), \(\varphi_{d} \equiv \sqrt{\varphi}\) and the constant \(C\) is given by
\[
C = \sqrt{\frac{1}{2} \frac{d^{2} F(m(\varphi_{d}), A_{\max})}{d A^{2}} \left( 1 + \frac{d F(m(\varphi_{d}), A_{\max})}{d m} \frac{d m(\varphi_{d})}{d \varphi} \right)}.
\]
Eq. S17 implies that
\[
\frac{d A(\varphi)}{d \varphi} = - \frac{C/2}{(\varphi - \varphi_{d})^{1/2}} + \text{regular terms},
\]
that is, \(A'(\varphi)\) has a square-root singularity at \(\varphi = \varphi_{d}\).

We show now that this square-root singularity is transmitted to compressibility. Expanding the expression for the pressure

Mariani et al. www.pnas.org/cgi/content/short/1500125112 2 of 3
Deriving Eq. S20 we obtain

$$\frac{dp(\hat{\phi})}{d\hat{\phi}} = -\frac{B(\hat{\phi}_d)}{2(\hat{\phi} - \hat{\phi}_d)^{2/\nu}} + \text{regular terms},$$

that is, the derivative $p'(\hat{\phi})$ of the pressure has a singularity in $\hat{\phi} = \hat{\phi}_d$ with the same critical exponent of $A'(\hat{\phi})$. This fact implies an overshoot in the pressure as the system escapes from the metastable state. Indeed, the same overshoot can be seen also in the state-following method (6), not only in the pressure vs. density plane, but also in the shear stress vs. shear strain plane.

Fig. S1. Radial distribution function $g(r)$ of the planted configuration at density $\phi_0 = 2.5$. 