As an initial guideline for experimental tests of the ideal glass transition (Random Pinning Glass Transition, RPGT) that shall be induced in a system by randomly pinning particles, we performed first-principle computations within the Hypernetted chain approximation and numerical simulations of a Hard Sphere model of glass-former. We obtain confirmation of the expected enhancement of glassy behaviour under the procedure of random pinning, which consists in freezing a fraction \( c \) of randomly chosen particles in the positions they have in an equilibrium configuration. We present the analytical phase diagram as a function of \( c \) and of the packing fraction \( \phi \), showing a line of RPGT ending in a critical point. We also obtain first microscopic results on cooperative length-scales characterizing medium-range amorphous order in Hard Sphere glasses and indirect quantitative information on a key thermodynamic quantity defined in proximity of ideal glass transitions, the amorphous surface tension. Finally, we present numerical results of pair correlation functions able to differentiate the liquid and the glass phases, as predicted by the analytic computations.

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A common feature of liquids deep below the melting point (supercooled) is the remarkably steep increase of relaxation time, until the system falls out of equilibrium at a conventional temperature \( T_\text{g} \). Since decades, it is present in the literature the claim of the possible presence of a phase transition \( T_\text{g} \), the ideal glass transition (IGT), underlying the dynamical arrest and located at a lower temperature \( T_K \). Despite the first formulation of a consistent phenomenological thermodynamic picture\(^6,7\), this intuition remained at length debated for the lack of other indicators of the imminent thermodynamic singularity. In this context, other theoretical perspectives based on dynamic or topological approaches, sometimes excluding the presence of any transition, have been proposed as alternative explanations of the sluggish dynamics\(^8,9\). In recent times, new important results have been obtained in the development of the thermodynamic scenario. We particularly refer on the one side to the first definition and detection of a new kind of cooperative length-scale\(^10,11\), called point-to-set \( l_{PS} \), and on the other side to the suggestion for a field theory description of the IGT in terms of a suitable large deviation function\(^11,12\) and the introduction of perturbative\(^13,14\) and non-perturbative\(^15,16\) fluctuations in this description. In view of a full fledged theory of glass-formers and quantitative predictions of their properties, these important conceptual advancements have been corroborated by the formulation of a microscopic theory\(^17,18\) inspired to classical first-principle computations techniques in liquid\(^19\).

In contrast with usual critical phenomena, the IGT is characterized by particularly severe critical properties, \textit{i.e.} an exponential growth of relaxation time accompanied by a much slower power law increase of the cooperative length. Hence, despite the numerous recent progresses, the direct study of the IGT and of its properties still remains too difficult to be achieved, leaving doubts on the full theoretical picture and on the existence of the IGT itself.

With the aim of giving an answer to these fundamental questions one of us recently proposed\(^20,21\) a procedure to check the predictions of the thermodynamic approach inducing in real systems a glass transition at moderate supercooling and more easily accessible than the IGT. The idea is as follows: freeze the position of a fraction \( c \) of particles of an equilibrated configuration and study the thermodynamics of the remaining free particles. This procedure should allow the observation of a remarkable growth of the relaxation time in the free-particles equilibrium dynamics and the eventual reaching of a glass transition, called Random Pinning Glass Transition (RPGT), as soon as the concentration of frozen particles reaches the critical value \( c_K \). As anticipated, this result should be valid in a full range of moderate and deep supercooling leading to the formation of a full line of RPGT, \( c_K(T) \), ending in the IGT at \( T_K \) and in a new glass critical point at high temperature. Moreover, we expect that the induced transitions are simpler to be studied because of the possibility of equilibrating the system in the glass phase, something inconceivable for the IGT.

On one side, this suggests that the way for a much easier test of the theory of IGT is open and calls for numerical\(^20,21\) and experimental studies of glass-formers with a fraction of frozen particles. On the other side, a microscopic first-principles theory of the RPGT is needed to give more detailed predictions on its physics and provide quantitative information useful in the planning stage of experimental and numerical tests.

In this rapid communication we report the results of a first-principle computation of the RPGT scenario following the method for a quantitative approach to...
IGT proposed in Ref.\cite{18} through an extension to glasses of the Hypernetted Chain (HNC) approximation of classical theory of simple liquids. We add first numerical simulation results in a bidisperse Hard Sphere system for the density-density correlation functions that we also obtained in the previous analytic computation. As glass-former model we chose an Hard Sphere system in 3 dimensions, for which a microscopic thermodynamic theory has already been developed\cite{21} in the unconstrained case. In HS models, particles interact through the usual HS potential \( \psi(r) = 0 \) for \( r \geq D_{i,j} \) and \( \infty \) for \( r < D_{i,j} \), where \( D_{i,j} \) is the sum of the radii of particles \( i \) and \( j \). Hence the control parameter ruling the approach to IGT is the density, \( \rho = N/V \) for a system with \( N \) particles in a volume \( V \), or the so called packing fraction \( \phi = 4\pi R^3 \rho / 3 \), the fraction of volume occupied by the particles (of radius \( R \)). Generalizations of the computation to thermal supercooled liquids models with different pair-potentials are straightforward.

As anticipated in the introduction, the emergence of non-trivial local fluctuations of amorphous order in proximity of the IGT and the microscopic computation of their spatial cooperative length-scales is a long standing open issue in IGT studies. Even if the HNC theory of glasses ideally deals with finite dimensional systems, it only provides microscopic results on density-density correlation function and quantitative predictions on global thermodynamic potentials. Despite several theoretical efforts\cite{31,32,31a,31b,31c} quantitative information on local correlation of glass order remained out of reach of this and other first principles approaches to realistic glass-formers. The present computation, combining together the HNC analytic approach with the pinning particle procedure, will finally overcome this limitation. In particular, not only the thermodynamic results of pinned systems will provide the first quantitative predictions on diverging length-scales of the unconstrained system but we will be also able to extract indirect results on a previously unreachable thermodynamic quantity (amorphous surface tension) expected to play a major role in the vicinity of the IGT.

The theoretical framework behind the thermodynamic picture of IGT is the Random First Order Transition (RFOT) theory. According to this theory, above a dynamical crossover density \( \phi_d \) (or below \( T_d \)), thermodynamics of dense granular systems (or deeply supercooled liquids) starts to be dominated by a large number of particularly stable amorphous configurations, and the equilibrium dynamics by rare jumps among them, corresponding to specific local rearrangements. A non-zero entropy of the \( N \) stable amorphous configurations can be defined as \( S_c = \text{lim}_{N \rightarrow \infty} \log(N)/N \neq 0 \) and is called configurational entropy. Upon further increasing of the density (or supercooling) the entropy of stable amorphous configurations decreases and vanishes at finite concentration (or temperature) leading in the RFOT theory to the occurrence at \( \phi_K \) (or \( T_K \)) of the IGT, a singularity of the thermodynamic entropy (or free-energy) potential. The classical theory of liquids based on diagrammatic expansion of the Morita-Hiroike (M-H) potential\cite{22,23}, also developed for obtaining simple HS liquid behavior at low packing fraction, has been adapted to capture the effects of this multi-state scenario and the occurrence of the IGT. In particular, among other approximation schemes adopted to compute pair correlation functions, HNC corresponds to a stationary point of a truncated M-H potential where two-line irreducible diagrams have been neglected\cite{23}.

A fundamental tool in the formulation of a HNC theory of glass-formers is the introduction of a number of copies (or replicas) of the system and the study of pair correlation functions between particles of different replicas. In practice a system is considered composed by a mixture of particles from different \( m \) copies of the original glass-former with positions given by 3d vectors \( \{ x_i^a \} \), where \( i \in [1,N] \) is the particle index, and \( a \in [1,m] \) is the replica index. Particles of the same replica interact through the usual pair-potential \( \psi(r) \) of the chosen model glass-former, while particles from different replicas do not see each other.

For \( m = 1 \) the problem can always be reconduced to the standard HNC liquid computation in terms of pair correlation function within a single replica \( g(x,y) = V^2/N^2 \sum_{i \neq j} \delta(x-x_i^a)\delta(y-y_j^b) \). In general, a new pair correlation function appears in the problem: \( \tilde{g}(x,y) = V^2/N^2 \sum_{i \neq j} \delta(x-x_i^a)\delta(y-y_j^b) \) with \( a \neq b \). According to the original ideas of replica approach\cite{33}, thermodynamic potentials of the glass-former as a function of \( \phi \) (or \( T \)) can be computed from the M-H potential of replicated system \( S_{m}^{M-H} \). The entropy of glass-former is \( s = \partial S_{m}^{M-H} / \partial m \big|_{m=1} \) and the configurational entropy \( S_c \) is \( S_c = -m^2 \partial [m^{-1} S_{m}^{M-H}] / \partial m \big|_{m=1} \).

In the liquid phase, pair correlation functions among different replicas are trivially equal to one, indicating that replicas are always completely independent. At variance, as soon as thermodynamics starts to be dominated by particularly stable configurations, beside the trivial liquid solution, a metastable solution (a new stationary point of the M-H truncated potential) with a non trivial \( g(x,y) \) structure appears. Particles of different replicas do not directly interact, hence the new inter-replica couplings are effectively generated by the glassy multi-state structure and force different copies of the system to lie in the same stable configuration.

To study RPGT, we need to deal with a Hard Sphere system where a fraction \( c \) of particles are frozen in an equilibrium reference configuration. We then need to study the thermodynamics of the remaining free particles replicated \( m \) times to probe the formation of a glassy multi-state structure. Finally we have to average over the equilibrium configurations of frozen particles. In practice, to realize this construction without breaking translational invariance, we will consider a mixture of \( N(1-c) \) particles replicated \( m \) times (\( m \) species), where particles interact only within the same specie \( \psi_{a,a}(r) = \psi(r) \), and
Eventually changes sign for \( c > c_c \) of \( c \) defined beyond the spinodal line. This also occurs for non-zero value for \( G \). Hence the stability of the corresponding liquid (\( \phi \)) and glass (\( G \)) phases shown in the phase diagram of Fig. 1. For \( \phi \in (\phi_d, \phi_K) \) and \( c = 0 \) it is \( s_L > s_G \), hence the \( L \) solution is stable. This also occurs for non-zero value of \( c \). However when \( c \) increases, the difference in entropy between the two phases decreases, vanishes at \( c_K(\phi) \), and eventually changes sign for \( c > c_K(\phi) \) where the \( G \) solution has become stable. Finally, the \( L \) phase cannot be defined beyond the spinodal line \( c_s(\phi) \).

\[
\log g(x, y) = \tilde{h}(x, y) - \tilde{c}(x, y) ,
\]

\[
\tilde{h}(x, y) - \tilde{c}(x, y) = h(x, y) - c(x, y) + (1 - c)\rho \int dw[h(x, w) - \tilde{h}(x, w)][c(w, y) - \tilde{c}(w, y)] .
\]

The first ones imply a solution \( g(r) \) independent from \( \tilde{g}(r) \) and identical to the simple liquid solution. The second ones admit two different solutions, \( \tilde{g}_L(r) \) and \( \tilde{g}_G(r) \), both present in some ranges of the control parameters \( \phi \) (or \( T \)) and \( c \). These two solutions encode respectively low trivial correlation between particles of different replicas induced by the presence of a fraction of \( N_c \) particles, and non-trivial high correlations effectively generated in the system when multi-state structure appears.

In the M-H entropy expression we deal with matrices of pair correlation functions \( \sqrt{\rho_\alpha \rho_\beta g_{\alpha \beta}} \) with only four different kinds of elements that, also assuming translational and rotational invariance, read: \( \rho_\alpha \rho_\alpha = c \rho g(\tau) \), if \( \alpha \neq 0 \) \( \rho_\alpha \rho_\beta = \rho_\alpha \rho_\alpha \rho_\alpha = \sqrt{c(1-c) \rho g(r)} \), and \( \rho_\alpha \rho_\alpha = (1-c) \rho g(r) \), and if also \( \beta \neq 0 \), \( \sqrt{\rho_\alpha \rho_\beta \rho_{\beta \alpha}} = (1-c) \rho g(r) \). Hence the entropy of glassformer, obtained from the M-H potential of replicated system \( s_m^{M-H} \), reads

\[
s[\phi, c; g, \tilde{g}] = -\frac{\rho}{2} \int 4\pi r^2 dr(1-c) \left[ (1+c)g(r)(\log(g(r)) - 1) + (1-c)\tilde{g}(r)(\log(\tilde{g}(r)) - 1) + (1+c)\psi(r)g(r) + 2 \right] + (7)
\]

\[
+ \frac{1}{2\rho} \int_q (1-c) \left[ -(1+c)\rho h + c \rho h + \frac{1}{2}(1+c)\rho^2 h^2 + \frac{1}{2}(1-c)\rho^2 \tilde{h}^2 + \rho \frac{ch + (1-c)\tilde{h}}{1 + \rho h} + \log \left(1 + (1-c)\rho(h - \tilde{h}) \right) \right] ,
\]

where \( h \) and \( \tilde{h} \) are functions of vector \( q \): the FTs of \( h(x - y) \) and \( \tilde{h}(x - y) \), and \( \int_q \) represents integration in the 3d momentum space. Through numerical iterative solution of Eqs. (9) we obtained: \( \tilde{g}_L(r) \) when starting from \( \tilde{g}(r) = 1 \) everywhere, and \( \tilde{g}_G(r) \) when starting from the non-trivial \( \tilde{g}(r) \) solution that appears for unconstrained systems between \( \phi_d \) and \( \phi_K \). We also computed their entropy values and hence the stability of the corresponding liquid (\( L \)) and glass (\( G \)) phases shown in the phase diagram of Fig. 1. For \( \phi \in (\phi_d, \phi_K) \) and \( c = 0 \) it is \( s_L > s_G \), hence the \( L \) solution is stable. This also occurs for non-zero value of \( c \). However when \( c \) increases, the difference in entropy between the two phases decreases, vanishes at \( c_K(\phi) \), and eventually changes sign for \( c > c_K(\phi) \) where the \( G \) solution has become stable. Finally, the \( L \) phase cannot be defined beyond the spinodal line \( c_s(\phi) \). Even if it deals with the discontinuous jump of the order parameter (the pair correlation function) between two solutions \( \tilde{g}_L(r) \) and \( \tilde{g}_G(r) \), the nature of the transition at \( c_K(\phi) \) is not simply first order. It has been already shown that, when particles are pinned from equilibrium configurations, the entropy (or more in general free-energy) mismatch between the two phases coincides with the configurational entropy of the constrained system (see appendices of Ref. (25)). Hence, \( c_K(\phi) \) indicates the occurrence of an entropy vanishing transition, the RPGT, with similar features to the IGT, except that amorphous order in ideal glass phase is unique and well known starting from the pinned particles equilibrium template. Another spinodal, \( c_4(\phi) \), the one of the phase \( G \), appears for \( \phi < \phi_d \), and the RPGT line continues in this low concentration regime, indicating that in a HS model the glass phase can be generated by pinning particles even if
it was not present in the unconstrained system. Hence, the observation of glassy behaviour including a dynamic transition and an eventual thermodynamic glass transition (RPGT-like) is expected even in not-prohibitively dense systems (or at moderate supercooling).

The two spinodals $c_d(\phi)$ and $c_s(\phi)$ slowly approach the transition line $c_K(\phi)$ when $\phi$ decreases, till the three lines meet in a critical point \( \{c^*, \phi^*\} \). For lower packing fraction, random pinning only induces trivial pair correlations among particles.

We now turn to the second major result of this work: the quantitative computation of cooperative length-scales in glass-formers. As anticipated, the HNC study of randomly pinned systems allows the first microscopic results on the cooperative length-scale of non-trivial glass fluctuations and an indirect evaluation of a key thermodynamic quantity of RFOT, the free-energy cost of the matching between different amorphous stable configurations. According to intuitive phenomenological arguments, pinning a finite fraction of particles leads to an extensive decrease of the configurational entropy of the original system $S_c(\phi)$. At least at small $c$, for the pinned system it should be (as it is confirmed by the results of the present computation) $S_c^P(\phi, c) \simeq S_c(\phi) - c Y(\phi)$. Several results can be obtained starting from this simple observation. First, the reaching of the RPGT occurs when $S_c^P(\phi, c)$ vanishes, hence when $c_K(\phi) \simeq S_c(\phi)/Y(\phi)$. From this point the glass phase is stable, hence the system is able to spontaneously reconstruct the template configuration starting from the local constraints imposed by pinned particles. This inevitably reveals in the template configuration the presence of a subtle medium-range correlation that extends over length-scales smaller than the typical distance $\xi$ between pairs of pinned particles at criticality: $\xi(\phi) \sim c_K^{-1/d}(\phi)$, where $d = 3$ is the dimensionality of the system. In quite perfect agreement with phenomenological scaling arguments, we obtain for $\xi(\phi)$ a simple inverse cubic square behavior (see Fig.2), ruled by the vanishing of $S_c(\phi) \sim \phi_K - \phi$, except for mild deviations in the pre-asymptotic range. Second, we notice that $Y(\phi)$ is a microscopic configurational entropy loss due to the locally imposed constraint, a quantity complementary to the interface free-energy cost between typical amorphous configurations that plays a fundamental role in RFOT. We can easily compute its value from a linear fit of the configurational entropy decrease due to small pinning, consistently finding that $Y$ is only defined where $S_c(\phi)$ exists, and hence above $\phi_d$, and it moderately increases when the IGT is approached, as it is shown in the inset of Fig.2. Third, a different cooperative length scale, called point-to-set, $l_{PS}$, was initially operatively defined by using an alternative pinning procedure where all the particles are pinned except those in a cavity of size $l$. Phenomenological arguments on that construction gave as a result $l_{PS} \sim Y(\phi)/S_c(\phi) \sim \xi(\phi)^d$. Through the present HNC computation, we can also evaluate this second length scale using the configurational entropy $S_c(\phi)$ of the unconstrained system and the coefficient $Y(\phi)$ of the linear decrease of configurational entropy $S_c^P(\phi, c)$ due to small pinning already computed. In Fig.2 the two cooperative length scales rescaled to one at $\phi_d$ are compared showing a much faster growth of $l_{PS}$, highlighting the difference between the two lengths, and indicating the convenience of the point-to-set procedure to reveal growth of amorphous order in real systems. Note that this result warns about possible important differences between apparently analogous procedures to de-
detect cooperative length scales.\(^{[22]}\)

For the numerical realization, we need to introduce polydispersity to prevent the crystallization. With this aim, we consider a 50 : 50 binary mixture of hard spheres of radius \(R_A\) and \(R_B = 1.4 R_A\), whose properties in the unconstrained case have been largely studied. We consider systems of 250 and 500 particles in a cubic simulation box of volume \(V = L^3\) with periodic boundary conditions, at fixed volume fractions \(\phi = 2 \pi \rho (R_A^3 + R_B^3) = 0.59, 0.595, 0.6\) and 0.605. As in the analytical calculations, we have two kind of particles: \(N(1-c)\) mobile particles, and \(cN\) pinned particles, whose positions will remain frozen during all the simulation. These pinned particles are chosen randomly from a thermalized configuration obtained for the unconstrained system.\(^{[33]}\) We simulate in a mesh of \(c\) values within 0 to 0.16. In addition, we consider 5 independent runs for each initial configuration.

As simulation method, we use a slightly modified version of the Event-Chain Monte Carlo (ECMC)\(^{[34]}\) to account for the \(cN\) pinned variables. Each ECMC move consists on a deterministic chain of events constructed as follows. Initially, one proposes a random particle among the \(N(1-c)\) mobile particles, and a vector \(\delta = \delta u\) (with \(\delta\) the modulus and \(u\) the unitary vector) chosen randomly within a sphere of radius \(\ell\). This particle is then displaced along \(u\) until the point where it strikes another sphere. At this point, there are two possible moves depending on the kind of particle stroked: (a) If the particle can move, this particle will also be displaced along \(u\) until it hits again a new particle. (b) On the contrary, if the particle is pinned and cannot move, we make the old sphere reboot and continue its linear motion but now on direction \(u' = (I - 2P)u\), being \(I\) is the identity matrix and \(P\) the projection matrix on the direction normal to the collision. This process is iterated until the total displacement of all the particles achieves the value \(\delta\). This algorithm allows us to accelerate the dynamics in the high density region about a factor 10 with respect to the standard Monte Carlo,\(^{[35]}\) which is the minimal factor to be able to decorrelate samples after the pinning process in a reasonable time, but yet not enough to be confident about the thermalization.

Finite-size studies did not give confirmation for the occurrence of the RPGT at \(\phi = 0.59\) and \(\phi = 0.595\), while first results at \(\phi = 0.6\) are encouraging. We can compute \(g(r)\) and \(\tilde{g}(r)\) for different values of \(c\). Since we deal with particles of two different sizes, we must consider the spatial correlation only among the different species, that is, \(AA, BB\), or alternatively, the mixed one, \(AB\). For the sake of clarity, we show in Figure 3 only the \(BB\) contribution (the one obtained for the biggest particles). As expected, \(g(r)\) is not affected by the pinning, while \(\tilde{g}(r)\) displays a very different behavior depending on the value of \(c\). In some cases (i.e. \(N = 250, \phi = 0.6\) and \(c = 0.02\)) first numerical simulation results from different dynamical histories in presence of the same pinning constraints show bimodal behavior for large time correlation with initial configuration. This is in favour of the presence of two competing \(L\) and \(G\) phases. We show in Fig 3 the corresponding pair correlation functions \(\tilde{g}_L(r)\) and \(\tilde{g}_G(r)\) that can be obtained comparing large times configurations from different histories with the initial template configuration. Even if \(\tilde{g}_L(r)\) and \(\tilde{g}_G(r)\) show well distinct behavior, their difference is not huge consistently with analytic results in the vicinity of the ending critical point of the RPGT line. More statistics (more dynamical histories and averages over initial template configurations) and finite-size scaling studies are needed to check the presence of the RPGT and the consequent confirmation of bistability.

We presented the microscopic results of first principle HNC computations and numerical simulations in a Hard Sphere model glass-former with a fraction of frozen particles.

The analytical results confirm expectations on the existence of a new kind of glass transition, called RPGT, induced by pinning particles and provide microscopic information on its occurrence in the \(\phi-c\) phase diagram. Limits of this approximations already in the unconstrained case lie in an overestimate of the dynamic transition’s packing fraction \(\phi_d\), an underestimate of the configurational entropy, and a systematic failure at high packing fraction \(\sim \phi_K\) where particles of different replicas overlap the most.\(^{[23]}\) On the other hand, results in the low packing fraction region around the critical point at the end of RPGT line in the constrained case, are expected to be more accurate, dealing with solutions \(\tilde{g}(r)\) that correspond to relatively low overlap among different replicas. Firstly microscopic results on non-trivial static cooperative length scales of glass order in this approach also derive from this computations covering the range of asymptotic and pre-asymptotic behavior.

Finally first numerical results on \(\tilde{g}(r)\) in a bi-disperse H-S model simulated with an optimized Monte-Carlo dynam-
ics have been presented.
Pair correlations among particles of the same replica are not changed by the presence of other replicas, nor by the presence of additional common non-replicated particles, as long as these are also equilibrated.

Trivial entropic terms due to single particle densities are neglected because they do not contribute to the RPGT. In particular, even in the $m = 1$ case, exchange entropy is affected by the fraction of pinned particles, but this is also the case for experiments or simulations.

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Note that this spinodal does not correspond to the spinodal of threshold states $c_{d_f}$ that can be obtained in dynamical analyses. Here we follow the fate of the equilibrated liquid phase, which disappear at lower concentration $c_s < c_{d_f}$ in pinned fully-connected Mean Field models.

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