

Universal behaviour of the glass and the jamming transitions in finite dimensions for hard spheres

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We investigate the glass and the jamming transitions of hard spheres in finite dimensions d , through a revised cell theory, that combines the free volume and the Random First Order Theory (RFOT). Recent results show that in infinite dimension the ideal glass transition and jamming transitions are distinct, while based on our theory we argue that they indeed coincide for finite d . As a consequence, jamming results into a percolation transition described by RFOT, with a static length diverging with exponent $\nu = 2/d$, which we verify through finite size scaling, and standard critical exponents $\alpha = 0$, $\beta = 0$ and $\gamma = 2$ independent on d .

1 Introduction

The transition between a fluid to an amorphous solid phase is common to many disordered systems, such as molecular liquids, colloids, granular materials and foams, and its understanding is one of the major problems in condensed matter. In a seminal paper¹, an universal jamming phase diagram was proposed to unify the transition of structural arrest of different systems, including the glass and the jamming transitions. However, within a mean field or the infinite dimensionality limit a distinction between the glass transition of liquids and the jamming transition of granular materials was posed in an analytical study of frictionless hard sphere particles^{3–7}. As illustrated in Fig. 1a, this approach predicts that on increasing the pressure, the equilibrium liquid line reaches a dynamical transition point, and then terminates at an ideal glass transition critical point, just like in the Random First Order Transition (RFOT) scenario first introduced by Kirkpatrick, Thirumalai and Wolynes⁸ and later developed by Wolynes and collaborators^{9,10}. At higher pressure, the mean field approach predicts a glass transition line that ends in the infinite-pressure limit at a jamming transition point. Here the gap between neighbour particles vanishes with a critical exponent, as the pressure diverges. Surprisingly this and other critical exponents are found⁵ to be consistent with those found numerically in

finite dimensions^{15,18}.

One important question is whether this overall scenario survives in finite dimensions. One possibility is that in finite dimensions this scenario disappears, the glass transition being a purely kinetic dynamic transition with no diverging static correlation length^{16,17}. Alternatively, according to RFOT, the dynamical transition^{19–21} becomes a crossover towards the ideal glass transition, where a static critical length associated to the cooperative rearranging regions^{8–10}, as originally introduced by Adam and Gibbs²², diverges. However, in this scenario it is not clear^{4,58} whether the ideal glass transition and the jamming transition would coincide⁶⁰ or not^{11,12} in finite dimension.

In this paper, we investigate the relation between the glass and the jamming transitions in finite dimensions, extending the Cell Theory of the Glass Transition²³, which reproduces the essential features of Free Volume Theory^{2,24,25}. Working within the RFOT scenario, we extend the cell theory taking into account the existence of cooperatively rearranging regions^{8–10}. As a consequence, local properties like the free volume distribution are modified due to the presence of the cooperative length. Starting from this free volume distribution, we give arguments indicating that for hard sphere systems the cooperative length diverges at the jamming transition density. As a consequence, as illustrated in Fig. 1b, the ideal glass critical density ρ_K coincides with the glass close packing density³, or ideal jamming density ρ_j , where the cooperative length diverges as $\xi \sim (\rho_j - \rho)^{-\nu}$, with $\nu = 2/d$ according to the RFOT. The experimental jamming transition realized via an out-of-equilibrium protocols^{11–14} is expected to occur at a protocol dependent volume fraction bounded by ρ_j , as also il-

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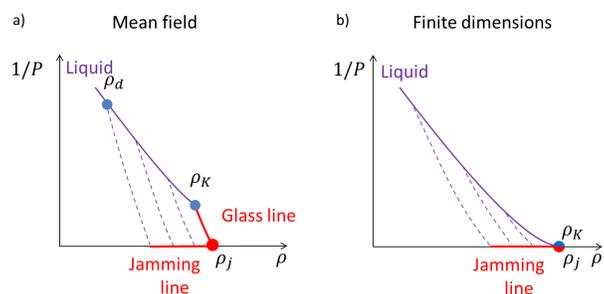


Fig. 1 Schematic phase diagram for a hard sphere system. The full line represents the ‘equilibrium’ equation of state within the metastable fluid phase, while dashed lines represent out-of-equilibrium compression protocols. The infinite pressure limit of these lines define the jamming line. Panel a illustrates mean field results elaborated from Fig. 4 of Ref.⁴, while panel b illustrates the finite dimensional scenario⁵⁸ supported by our results. Here the ideal glass transition critical density ρ_K coincides with an ideal jamming critical density ρ_j , both being located at the end of an equilibrium line.

illustrated in the figure. The identification of the glass and of the jamming transitions is supported by the fact that ξ results proportional to the hyperuniform length, considering that hyperuniformity has been proposed as an essential property of the maximum jamming density^{30–33}.

We checked the prediction for ν via large-scale simulations using finite size scaling at the jamming transition, where we find numerical values in $2d$ and $3d$ in excellent agreement with the predicted exponent $\nu = 2/d$. This critical point can be described as a mixed order percolation transition, with the order parameter jumping discontinuously at the transition, $\beta = 0$, the mean cluster size diverging with exponent $\gamma = 2$, and the number of clusters of size ξ vanishing with an exponent $2 - \alpha = 2$ independent on the dimensionality. We name this percolative description of the RFOT theory Random First Order Percolation Transition, RFOPT. This scenario is quite different from other mixed-order percolation transition, such as the bootstrap percolation^{26–29}. The hallmark of RFOPT is the presence of critical exponents that do not depend on the dimensionality, which is a typical property of the jamming transition.

2 Cell Theory

We start by shortly reviewing the Cell Theory of the Glass transition^{23,35,36}, that combines lattice theories of liquids³⁷ and the ideas of inherent structures, free-volume theory, and geometrical packing properties to understand the complex dynamics of glass-forming liquids, granular packings, and amorphous solids. In the lattice theory of liquids³⁷, the system is

divided in N identical cells each corresponding to the unitary cell of the underlying crystal. Analogously, in the cell theory of glass-forming liquids, the system is divided in N Voronoi cells corresponding to the generic underlying inherent state, but one also considers that there are Ω statistically independent inherent states. Consequently, the partition function of a system of N hard sphere particles in a volume V is:

$$Z = \sum_{\{N(\mathbf{n})\}} \Omega(\{N(\mathbf{n})\}) e^{-\beta F(\{N(\mathbf{n})\})}, \quad (1)$$

where

$$F(\{N(\mathbf{n})\}) = -kT \sum_{\mathbf{n}} N(\mathbf{n}) \left[\ln \frac{v_f(\mathbf{n})}{\Lambda^d \mathcal{P}(\mathbf{n})} \right], \quad (2)$$

is the free energy of the inherent states^{23,35,36}, Λ is the de Broglie length, \mathbf{n} is a discrete index referring to the properties of the cell, $N(\mathbf{n})$ the number of cells sharing the same index \mathbf{n} , $v_f(\mathbf{n})$ the ‘free volume’ associated with a particle in a cell³⁷. $\mathcal{P}(\mathbf{n})$ is the probability to find a cell with \mathbf{n} that is single-occupied. The free volume³⁷ of a particle is the volume the particle can explore, averaged over all possible configurations of the other particles, in a system restrained to single occupancy of cells. The quantity $\Omega(\{N(\mathbf{n})\})$ in Eq. 1 counts the number of distinct space-partitions (associated with the inherent states) made with the same set of $\{N(\mathbf{n})\}$. The key elements to be estimated in Eq. 2 are $\mathcal{P}(\mathbf{n})$ and $\Omega(\{N(\mathbf{n})\})$. At high density, which will be always considered throughout the paper, all Voronoi cells of the underlying inherent structure are essentially singly occupied and $\mathcal{P}(\mathbf{n}) \sim 1$. $\Omega(\{N(\mathbf{n})\})$ can be estimated^{23,35,36} as the number of distinct configurations that can be made by positioning in different ways the N cells distributed in groups of $N(\mathbf{n})$, namely $\Omega(\{N(\mathbf{n})\}) = N! / \prod_{\mathbf{n}} N(\mathbf{n})!$. The partition function, Eq. 1, can be calculated via a saddle-point approximation, where the sum over all the distributions $\{N(\mathbf{n})\}$ is replaced with the contribution from a distribution $N^*(\mathbf{n})$ which minimizes the total free energy $\ln Z$. From this^{23,35,36}, it is possible to derive the distribution of the free volumes, that in the continuum limit becomes $p(v_f) = \frac{4}{\Gamma(2)} \frac{v_f}{\langle v_f \rangle^2} \exp\left(-2 \frac{v_f}{\langle v_f \rangle}\right)$, where $\langle v_f \rangle$ is the average free volume per particle and $\Gamma(\cdot)$ is the Gamma function. The distribution essentially coincides with the distribution originally evaluated within the free volume theory^{2,24,25}, which predicts a simple exponential form.

3 Extended Theory

The cell theory can be extended to take into account the presence of the cooperatively rearranging regions of RFOT^{8–10}, one could identify through a set-to-point correlation approach⁴⁹. Within RFOT the system is partitioned in droplets

of linear size ξ that, as in first-order transitions, have a free energy of nucleation containing a volume term plus a surface term. In standard nucleation theory the surface term is proportional to ξ^{d-1} , while in RFOT it is argued that the surface term is proportional to ξ^θ with $\theta = d/2$, d being the space dimension (see also^{38,39} for further elaboration and a discussion of other possible values of θ). The theory predicts that the configurational entropy s_c vanishes as the size of the droplet diverges $s_c \sim 1/\xi^{d-\theta}$, while the relaxation time diverges exponentially. Since the total entropy inside the droplet is $\xi^d s_c \simeq \xi^\theta$, according to RFOT the number of effective degree of freedom of a droplet scales as ξ^θ . The overall number of degree of freedom, which equals the number of droplets times the degree of freedom per droplet, is thus reduced by a factor $\lambda = (\xi/r_0)^{d-\theta}$, with r_0 a characteristic size such that $\rho r_0^d = 1$, with ρ being the particle density. Within the cell theory, this leads to a reduction in the number of configurations Ω , appearing in the partition function, Eq. 1, which now becomes $\Omega(\{N(\mathbf{n})\}) = \frac{(N/\lambda)!}{\prod_{\mathbf{n}} (N(\mathbf{n})/\lambda)!}$, where $(N(\mathbf{n})/\lambda)$ physically represents the number of particles which are able to move characterized by the same cell index \mathbf{n} . Using Stirling's approximation:

$$\ln \Omega(\{N(\mathbf{n})\}) \simeq - \sum_{\mathbf{n}} \frac{N(\mathbf{n})}{\lambda} \ln \frac{N(\mathbf{n})}{N}. \quad (3)$$

Following the same procedure as for the case $\lambda = 1$ we derive a new free volume distribution

$$p(v_f) = \frac{k^k v_f^{k-1}}{\Gamma(k) \langle v_f \rangle^k} \exp\left(-k \frac{v_f}{\langle v_f \rangle}\right), \quad (4)$$

with⁴⁰ $k = 1 + \lambda$. From Eq. 1, Eq. 3 and Eq. 4 we find:

$$\frac{\ln Z}{N} = \int p(v_f) \ln \frac{v_f}{\Lambda^d} dv_f + s_c, \quad (5)$$

where $s_c = -\frac{B}{\lambda}$ is the configurational entropy, Eq. 3, with $B = \int p(v_f) \ln p(v_f) dv_f$ being a smooth function of $\langle v_f \rangle$.

Since $\lambda = (\xi/r_0)^{d-\theta}$, we recover $\xi \propto s_c^{\frac{1}{\theta-d}}$ as in RFOT. For molecular liquids Kauzmann assumed⁴², $s_c \propto (T - T_k)$. In hard sphere systems, where the control parameter is the density and not the temperature, one assumes $s_c \propto (\rho_K - \rho)$. With this assumption, the critical behaviour of the correlation length is $\xi \propto (\rho_K - \rho)^{-1/(d-\theta)}$ and, for $\theta = d/2$, $\nu = 2/d$.

The free volume distribution Eq. 4 tends to a delta function in the limit $k \rightarrow \infty$, i.e. $s_c \rightarrow 0$. In this limit, $\xi \rightarrow \infty$ and $\rho \rightarrow \rho_k$. Accordingly, if ξ diverges for all values of the density between ρ_k and ρ_j , then the free volume distribution is a delta function in this density interval. This scenario is in principle possible, also considering how the free volume is defined within the cell theory of liquids, but it is contrary to

the expectation that, due to the disorder of the system, only at jamming the free volume distribution would be a delta function. We therefore argue that the volume distribution is a delta function only at jamming. This assumption implies $\rho_j = \rho_K$, and

$$\xi/r_0 \sim (\rho_j - \rho)^{-2/(d-\theta)}. \quad (6)$$

We stress that the coincidence of the jamming transition and the glass transition does not depend on the assumed value of θ , which is an important point as the value of θ is controversial and of difficult experimental determination. Note that, since $p(v_f)$ approaches a δ -function for $\langle v_f \rangle \rightarrow 0$, our approach predicts that the ideal jammed configuration has no rattlers, as in mean field⁴¹.

From Eq. 6 one determines the dependence of k on ρ and therefore, assuming⁴³ $\langle v_f \rangle^{1/x} = A(\rho_j - \rho)$ where A is a constant, the dependence of k on $\langle v_f \rangle$. This allows to derive the equation of state from Eq. 4 and Eq. 5, $P = k_B T \left(\partial \ln Z / \partial V \right)_{N,T}$,

$$\frac{P}{Nk_B T} = \frac{x}{V - V_J}. \quad (7)$$

Here $\rho_j = N/V_j$ is the jamming density corresponding to infinite pressure. Free volume theory⁴⁴ predicted Eq. 7 with $x = d$.

From Eq. 7 we find the compressibility to vanish at the jamming transition as $\kappa_T \sim (\rho_j - \rho)^2$. Using Eq. 6 it follows that the relation between the compressibility and the cooperative length is given by $\kappa_T \sim (\xi/r_0)^{-d}$. Interestingly the vanishing of the compressibility in monodisperse jammed particles has been linked to the concept of hyperuniformity. More precisely close to the jamming glass state in 3d it was found $\kappa_T \sim (\xi_{DCF})^{-3}$, where ξ_{DCF} , is a diverging length defined through to the direct pair correlation function³⁰⁻³². This implies that in 3d the hyperuniform length and the cooperative length are proportional close to the jamming glass transition $\xi \sim \xi_{DCF}$. While the link between jamming and hyperuniformity has been questioned⁵⁹ our results support the speculation by Atkinson et al.³³ according to which exact hyperuniformity occurs in packings with no rattlers.

We now examine how the predictions of the extended cell theory compare to available numerical data. First, we consider the prediction $\rho_k = \rho_j$, and the related equation of state of Eq. 7. We remind that ρ_k is the ideal-glass transition density identified from the divergence of the cooperative correlation length ξ , while ρ_j is the density at which the pressure diverges, along the metastable fluid branch. A precise measurement of both ρ_k and ρ_j is made difficult by the need of equilibrating the system, as the divergence of the correlation length implies the growth of the relaxation time. A numerical investigation of the dependence of the cooperative correlation length on the pressure, however, found results consistent

with the correlation length diverging in the infinite pressure limit, and thus consistent with the $\rho_k = \rho_j$ prediction⁷¹. Previous numerical investigations of the equation of state along the equilibrium metastable branch^{60,65} for monodisperse hard sphere support the equation of state of Eq. 7. As a side remark, we note that Eq. 7 is quite robust, as it is also recovered during the slow decompression of jammed packings produced with a fast compression, whose jamming density is not the maximal one^{43,45}. The extrapolated volume fraction at which the pressure diverges along the metastable fluid branch is found to be $\phi_j = 0.644 \pm 0.005$ ⁶⁵ and $\phi_j = 0.640 \pm 0.006$ ⁶⁰, and consistent with the maximal volume fraction of disordered jammed configurations prepared via diverse out-of-equilibrium procedure^{14,61–64}. This supports the idea that the pressure along the metastable equilibrium branch diverges at the upper bound of the j-line, as in Fig. 1b. Of course, numerical results are not a proof. In particular, we note that the numerical estimates of the pressure/density at which the correlation length diverges are notoriously difficult. In addition, the estimate of ρ_j need to be considered with care as it is difficult to equilibrate hard sphere systems at high densities, because partial ordering might intervene.

The other predictions of our theory, namely the form of the free volume distribution along the metastable fluid branch, and its convergence to a delta function as $\rho \rightarrow \rho_k$, which implies the absence of rattlers, cannot be directly tested against literature data. Indeed, previous investigations considered the free volume distribution of the particles averaging over different configurations, in the liquid phase^{68–70} or in out of equilibrium high density states⁴³, while within the cell theory the free volume of a particle is the average over the configurations of a same inherent structure. Since these two measurements give different results for crystals, unless the system is close packed, we expect them to also give different results along the metastable liquid branch, unless the system is at the ideal transition, where according to both definition the free volume distribution is a delta in zero, and the system has no rattlers.

We also notice that in monodisperse systems the fraction of rattlers along the j-line has been found⁴³ to vary from 1.7% at $\phi = 0.6392$ to 1.6% at $\phi = 0.6419$, in agreement with the possibility that the number of rattlers vanishes at ρ_j . However, a detailed investigation of this issue should be carried out. In this respect, we remind that jammed configurations are produced through out-of-equilibrium protocols, so that the fraction of rattlers is also protocol dependent⁷². For instance, for large system sizes the fraction of rattlers of jammed packings of hard-sphere systems converges towards 0.025–0.030, for packings prepared using the Lubachevsky-Stillinger algorithm, and towards 0.015, for packings prepared using the Torquato-Jiao protocol³⁴.

4 Random First Order Percolation Transition

The above results allow to interpret the jamming glass transition as a percolation transition, we name Random First Order Percolation Transition. This is a percolation transition of compact clusters⁴⁹ of linear dimension ξ and fractal dimension $D = d^{46–48}$. The size s^* of the critical cluster is given by $s^* \sim \xi^d$. As the transition is approached the number density of critical clusters vanishes as ξ^{-d} , and the percolation probability jumps discontinuously from 0 to 1. Adapting the standard scaling ansatz^{51–53} for the cluster size distribution $n(s)$ to this peculiar random first-order percolation, we obtain $n(s) \sim 1/s^\tau f(s/s^*)$, where $f(x)$ is a rapidly decreasing function for $x \gg 1$, that scales as $f(x) \propto x^{-\tau}$ with $\tau = d/D + 1 = 2$ for $x \ll 1$. The number density of clusters scales as $\int n(s) ds \propto \xi^{-D(\tau-1)} \propto (\rho_j - \rho)^{2-\alpha}$. Thus, given Eq. 6, and assuming $\theta = d/2$ (see below for the influence of the value θ), we find $\alpha = 0$. The mean cluster size⁵¹ $S = \sum s^2 n(s) / \sum s n(s)$ diverges at jamming as a power law $S \sim (\rho_j - \rho)^{-\gamma}$ with $\gamma = \nu(d+D)/2 = 2$. The critical exponent associated to the order parameter is $\beta = \nu(d-D) = 0$. Summarizing, these exponents satisfy the scaling and hyperscaling law:

$$2\beta + \gamma = 2 - \alpha = d\nu. \quad (8)$$

Interestingly we have $\alpha = 0$, $\beta = 0$, $\gamma = 2$ which are independent on the dimensionality. A similar independence of the critical exponents on the dimensionality characterizes the jamming transition. The only exponent depending on the dimensionality is ν that equals $2/d$. This exponent can be estimated via standard finite-size scaling of the jamming transition density, $\Delta\rho(N) = \rho_j^* - \rho_j(N)$, where ρ_j^* is the estimated jamming density in the thermodynamic limit, and of the width of the jamming probability distribution, $\sigma(N)$, that scale as $\Delta\rho \propto \sigma \propto N^{-1/d\nu}$. It is in principle impossible to check this prediction, as it refers to the equilibrium jamming point which is not accessible in the simulations. However, one might expect the critical exponent to be the same for all jamming volume fractions. Literature investigations of these scaling relations^{14,18,54,58} conducted at the smallest value of the jamming volume fraction along the J-line do not unambiguously fix the value of ν ⁵⁵. We have evaluated the probability distribution of the jamming thresholds through large-scale simulations, using different jamming protocols to access different volume fractions along the J-line. Our results, reported in Fig. 2, show that $\Delta\rho \propto \sigma \propto N^{-1/2}$ in both $2d$ and $3d$, consistently with our theoretical prediction, $\nu = 2/d$.

We stress that this scenario refers to the transition as approached from the unjammed phase, the other side of the transition being not accessible in hard-sphere systems. In soft sphere systems, one might observe different geometrical exponents above the transition should the jammed and the unjammed phase be separated by a singularity⁵⁶. In addition,

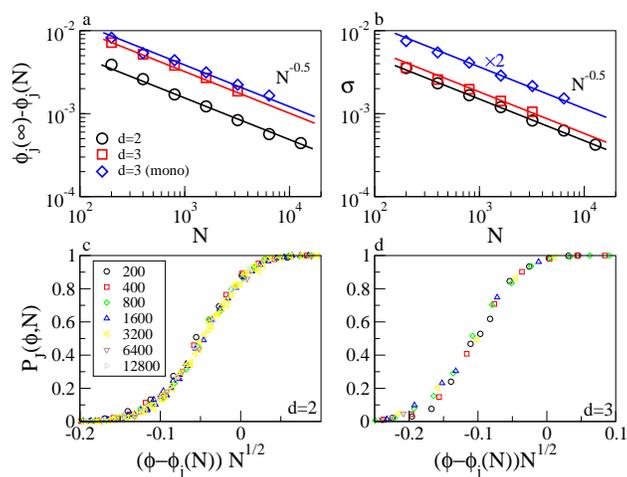


Fig. 2 Finite size scaling of the jamming probabilities of soft particles interacting via a Harmonic potential, in two and three dimensions. We show data for a mixture of particles with size ratio 1.4 and, in three dimensions, also for a monodisperse system. The jamming probability is computed as the average over $10^2 - 10^3$ independent configurations for every system size N and volume fraction $\phi = \rho v_p$, with v_p average particle volume. The configurations are prepared minimizing the energy with the CG protocol^{18,54}. The distributions are well approximated by an error function, from which we extract a size dependent jamming volume fraction, $\phi_j(N)$, and a width, $\sigma(N)$. We find $\phi_j(\infty) - \phi_j(N) \propto N^{-1/2}$, where $\phi_j(\infty)$ is the system and protocol dependent jamming volume fraction in the thermodynamic limit, as illustrated in panel a, and $\sigma(N) \propto N^{-1/2}$, as illustrated in panel b. Panels c and d illustrate the collapse of the jamming probability distributions. Analogous results are obtained for monodisperse systems, in three dimensions, as well using a different preparation protocol¹⁴ to explore the J-line.

above the transition other exponents, satisfying their own scaling relations, describe the elastic response of the system⁵⁷.

The percolation exponents depend on the value of θ , in particular for a generic value of θ one finds $\alpha = 2 - d/(d - \theta)$, $\gamma = d/(d - \theta)$, $\nu = 1/(d - \theta)$. However the exponents still satisfy the scaling and hyperscaling relation of Eq. 8. In any case the value $\nu = 2/d$ suggested by the finite size scaling reported in Fig. 2 are consistent with $\theta = d/2$ as assumed.

5 Conclusions

In conclusion using a cell theory previously developed, combined with the RFOT approach, we have suggested that for a monodisperse hard sphere system in finite dimension the ideal glass transition, where the cooperative length of the RFOT diverges, coincides with the ideal jamming transition which occurs at infinite pressure at the end of an equilibrium line where the jamming density is maximal without rattlers, as in

Fig. 1b. Following^{9,22}, the relaxation times τ diverges a la Vogel-Fulcher on approaching the jamming glass critical density, $\frac{\tau}{\tau_0} = \exp(A/(\rho_j - \rho))$. Using the properties of the RFOT theory we have been able to describe this glass jamming critical point as a Random First Order Percolation Transition. This allows rationalizing the critical behaviour of the jamming transition in terms of an order parameter which jumps discontinuously, a critical length with a critical exponent dependent on the dimensionality, and all other critical exponents independent on the dimensionality. These exponents satisfy scaling laws typical of critical phenomena, Eq. 8. We note that it is possible to associate other critical exponents to the jamming transition. This is common within percolation theory where, besides usual critical exponents obeying standard scaling laws, many other critical exponents are introduced, related to quantities, like shortest path, backbone, elastic properties and so on⁵¹⁻⁵³, reflecting structural properties of the critical clusters. Some of the theoretical predictions, such as the coincidence between ρ_k and ρ_j , are supported by numerical results, while others are currently difficult to test. Thus, our paper may stimulate other research to prove or disprove some of the predictions we have shown to derive from the unification of the free volume and of the RFOT theory. If future results disprove these predictions then some of the basic ingredients of the proposed approach, such as the free volume theory, the RFOT, or some of our assumptions, must be reconsidered. An interesting open question ahead is the generalization of this scenario to polydisperse systems, that might satisfy a different equation of state¹² and appears to have rattlers at their maximum jamming density¹³, as well as to describe systems of non-spherical particles⁶⁷. In summary, our work provides insights that change the current theoretical interpretation of the relation between the glass and the jamming transitions, supporting the original suggestion of Ref. 1, and proposing a novel percolative interpretation of this transition inspired by RFOT.

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