Theory of Amorphous Packings of Binary Mixtures of Hard Spheres

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(Received 19 February 2009; revised manuscript received 29 March 2009; published 13 May 2009)

We extend our theory of amorphous packings of hard spheres to binary mixtures and more generally to multicomponent systems. The theory is based on the assumption that amorphous packings produced by typical experimental or numerical protocols can be identified with the infinite pressure limit of long-lived metastable glassy states. We test this assumption against numerical and experimental data and show that the theory correctly reproduces the variation with mixture composition of structural observables, such as the total packing fraction and the partial coordination numbers.

DOI: 10.1103/PhysRevLett.102.195701 PACS numbers: 64.70.Q−, 05.20.−y, 61.43.−j

Amorphous packings of hard spheres are ubiquitous in physics: they have been used as models for liquids, glasses, colloidal systems, granular systems, and powders. They are also related to important problems in mathematics and information theory, such as digitalization of signals, error correcting codes, and optimization problems. Moreover, the structure and density (or porosity) of amorphous multicomponent packings are important in many branches of science and technology, ranging from oil extraction to storage of grains in silos.

Despite being empirically studied for at least 60 years, amorphous packings still lack a precise mathematical definition, due to the intrinsic difficulty of quantifying "randomness" [1]. Indeed, even if a sphere packing is a purely geometrical object, in practice dense amorphous packings always result from rather complicated dynamical protocols: for instance, spheres can be thrown at random in a box that is subsequently shaken to achieve compactification [2], or they can be deposited onto a random seed cluster [3]. In numerical simulations, one starts from a random distribution of small spheres and inflates them until a jammed state is reached [4,5]; alternatively, one starts from large overlapping spheres and reduces the diameter in order to eliminate the overlaps [6–9]. In principle, each of these dynamical prescriptions produces an ensemble of final packings that depends on the details of the procedure used. Still, very remarkably, if the presence of crystalline regions is avoided, the structural properties of amorphous packings turn out to be very similar. This observation led to the proposal that "typical" amorphous packings should have common structure and density; the latter has been denoted random close packing density. The definition of random close packing has been intensively debated in the last few years, in connection with the progress of numerical simulations [1,10].

Nevertheless, the empirical evidence, that amorphous packings produced according to very different protocols have common structural properties, is striking and calls for an explanation. This is all the more true for binary or multicomponent mixtures, where in addition to the usual structural observables, such as the structure factor, one can investigate other quantities such as the coordination between spheres of different types, and can study their variation with the composition of the mixture.

In earlier attempts to build statistical models of packings, only the main geometrical factors, such as the relative size and abundance of the different components, were taken into account [11–13]. More precisely, these models focus on a random sphere in the packing and its first neighbors, completely neglecting spatial correlations beside the first shell and all the global geometric constraints. This already accounts for the main qualitative structural properties of random packings. However, in order to obtain a quantitative description, some free parameters have to be introduced and adjusted to match with experimental data.

To go beyond these simple models, many authors proposed that random packings of hard spheres can be thought of as the infinite pressure limit of hard sphere glasses [14–20]. This is very intuitive since a glass is a solid state in which particles vibrate around amorphous reference positions, and vibrations are reduced on increasing pressure. A typical algorithm attempting to create a random packing starts at low density and compresses the system at a given rate. During this evolution, when the density is high enough, relaxation becomes more and more difficult until at some point the system is stuck into a glass state [19,20]; at this point further compression will only reduce the amplitude of the vibrations. In a nutshell, this is why amorphous packings can be identified with glasses at infinite pressure.

The main advantage of this identification, if it holds, is that a glass is a metastable state that has a very long lifetime; therefore, its properties can be studied using concepts of equilibrium statistical mechanics. In this way a complicated dynamical problem (solving the equations of motion for a given protocol) is reduced to a much more simple equilibrium problem. In [18,20] it was shown, in the case of monodisperse packings, that this strategy is very effective since it allows the computation of structural properties of random packings directly from the Hamiltonian of the system, without free parameters and in a controlled statistical mechanics framework. Note that the existence of an equilibrium glass transition in hard sphere systems (or in other words the existence of glasses with an infinite lifetime) has been questioned [5,21]. Although very interesting, this problem is not relevant for the present discussion since we are only interested in long-lived metastable glasses that trap dynamical algorithms. At present it is very well established by numerical simulations [22,23] that for system sizes of $N \lesssim 10^4$ particles and on the time scales of typical algorithms, metastable glassy states exist, at least in $d \geq 3$. This is enough to compare with most of the currently available numerical and experimental data. Finally, the relation of this approach to special packings such as the maximally random jammed state [1] and the J point [8] has been discussed in detail in [20].

The aim of this Letter is to extend the theory of [18,20] to binary mixtures. This allows the quantitative comparison of the predictions of the theory and the results of numerical simulations. We will focus, in particular, on the variation of density and local connectivity as a function of mixture composition. These results constitute, in our opinion, a stringent test of the assumption that random packings reached by standard algorithms can be identified with infinite pressure metastable glasses.

Theory.—The equilibrium statistical mechanics computation of the properties of the glass is based on standard liquid theory [24] and on the replica method [17,25] that has been developed in the context of spin glass theory [26,27]. For monodisperse hard spheres, it has been described in great detail in [20]. The extension to multicomponent systems is straightforward following [28]; details are given in Ref. [29].

Here we just recall some features of this approach, based on simple physical considerations. The basic assumptions of the method are (i) that crystallization and phase separation are strongly suppressed by kinetic effects so that the liquid can be safely followed at high density, and (ii) that at sufficiently high density, the liquid is a superposition of a collection of amorphous metastable states. Namely, in the liquid, the system spends some time inside one of these states, and sometimes undergoes a rearrangement that leads to a different state [30]. Each state is characterized by its vibrational entropy per particle, denoted by s, and the number of such states is assumed to be exponential in N, so a configurational entropy is defined as $\Sigma(\varphi, s) = N^{-1} \log \mathcal{N}(\varphi, s)$, with $\mathcal{N}(\varphi, s)$ being the number of states having entropy s at density φ. On increasing the density, the liquid is trapped for longer and longer times into a metastable state, until at some point the transition time becomes so long that for all practical purposes the system is stuck into one state; it then becomes a glass. To compute the properties of the glassy states, the central problem is to compute the function $\Sigma(\varphi, s)$. This can be done by means of a simple replica method introduced by Monasson [27]. One introduces m copies of each particle, constrained to be close enough, in such a way that they must be in the same metastable state. Then the total entropy of the system of m copies is given by $\mathcal{S}(m, \varphi|s) = ms + \Sigma(\varphi, s)$; the first term gives the entropy of the m copies in a state of entropy s, while the second term is due to the multiplicity of possible states. The total entropy of the system at fixed density φ is obtained by maximizing over s; i.e.,

$$\mathcal{S}(m, \varphi) = \max_s [\Sigma(\varphi, s) + ms] = \Sigma(\varphi, s^*) + ms^*, \quad (1)$$

where $s^*(m, \varphi)$ is determined by the condition $\partial_s \Sigma(\varphi, s) = m$. Then it is straightforward to show that

$$\begin{gathered} s^*(m, \varphi) = \partial_m \mathcal{S}(m, \varphi), \\ \Sigma[\varphi, s^*(m, \varphi)] = -m^2 \partial_m[\mathcal{S}(m, \varphi)/m]. \end{gathered} \quad (2)$$

The knowledge of $\mathcal{S}(m, \varphi)$ allows the reconstruction of the curve $\Sigma(\varphi, s)$ for a given density by a parametric plot of Eq. (2) by varying m. The function $\Sigma(\varphi, s)$ gives access to the internal entropy and the number of metastable glassy states; from this one can compute their equation of state, i.e., the pressure as a function of the density. In particular, for each set of glassy states of given configurational entropy Σ_j, one can compute the density φ_j (jamming density) at which the glassy states' pressure diverges. Since φ_j turns out to depend (slightly) on Σ_j, a prediction of the theory is that different glasses will jam at different density: amorphous packings can be found in a finite (but small) interval of density [19,20].

Results for binary mixtures.—The details of the computation of the function $\mathcal{S}(m, \varphi)$ for a general multicomponent mixture, based on [20], can be found in Ref. [29]. Here we consider a binary mixture of two types of spheres $\mu = A, B$ in a volume V, with different diameter D_μ and density $\rho_\mu = N_\mu/V$. We define $r = D_A/D_B > 1$ the diameter ratio and $x = N_A/N_B$ the concentration ratio; $V_3(D) = \pi D^3/6$ the volume of a three-dimensional sphere of diameter D; $\varphi = \rho_A V_3(D_A) + \rho_B V_3(D_B)$ the packing fraction; and $\eta = \rho_B V_3(D_B)/\varphi = 1/(1 + xr^3)$ the volume fraction of the small (B) component.

Once an equation of state for the liquid has been chosen, the jamming packing fraction φ_j is given in terms of Σ_j by the solution of $\Sigma_j(\varphi) = \Sigma_j$. The average coordination numbers at φ_j are denoted $z_{\mu\nu}(\varphi_j)$, but we checked that their variations with φ_j are negligible. We used in $d = 3$ the equation of state proposed in [31], using the Carnahan-Starling equation for the monodisperse system [24]. The latter, as well as $\Sigma_j(\varphi)$ and $z_{\mu\nu}(\varphi_j)$, are given, respectively, in Eqs. (19), (14), and (17) in Ref. [29].

Numerical simulations.—We produced jammed packings of binary mixtures of $N = 1000$ hard spheres using the code developed by Donev and co-workers [32,33]. In this algorithm spheres are compressed uniformly by increasing their diameter at a rate $dD/dt = 2\gamma$, while event-driven molecular dynamics is performed at the same time. In order to obtain a perfectly jammed final packing, the later stages of compression must be performed very slowly. On the other hand, at low density slow compression is a waste of time, since the dynamics of the system is very fast. Following [34], we find a good compromise by performing a four stages compression: starting from random configurations at $\varphi = 0.1$, (i) the first stage is a relatively fast compression ($\gamma = 10^{-2}$) up to a reduced pressure $p = \beta P/\rho = 10^2$; then we compress at (ii) $\gamma = 10^{-3}$ up to $p = 10^3$, (iii) $\gamma = 10^{-4}$ up to $p = 10^9$, and (iv) $\gamma = 10^{-5}$ up to $p = 10^{12}$. The first stage terminates at a density $\varphi \sim 0.6$, and is fast enough to avoid crystallization and phase separation. During the following stages the system is already dense enough to stay close to the amorphous structure reached during the first stage. Still, little rearrangements (involving many particles) are possible and allow reaching a collectively jammed final state [34]. In the final configurations, we observe a huge gap between contacting (typical gap $\sim 10^{-11}\ D$) and noncontacting (typical gap $\gtrsim 10^{-6}\ D$) particles. We then say that two particles are in contact whenever the gap is smaller than $10^{-8}\ D$. Typically, a small fraction ($\lesssim 5\%$ of the total) of rattlers, i.e., particles having less than 4 contacts, is present. Once these are removed, the configuration is isostatic (the total number of contacts is $6N$) within 1% accuracy.

Comparison of theory and numerical/experimental data.—During the four stages of compression, the pressure initially follows the liquid equation of state up to some density close to the glass transition density [20,35,36]. Above this density, pressure increases faster and diverges on approaching jamming at φ_j. The exact point where this happens depends on compression rate. This is a nice confirmation of a prediction of the theory that different glassy states jam at different density; it was already observed in [5,34] and recently discussed in great detail in [23,37]. Within the theory φ_j is related to Σ_j, the value of configurational entropy at which the system falls out of equilibrium; hence there is one free parameter, Σ_j, that depends on the compression protocol. The equation of state of the glass obtained numerically with our protocol corresponds within our theory to $\Sigma_j \sim 1.5$. We decided to use the value $\Sigma_j = 1.7$ that gives the best fit to the numerical data. This is consistent with previous observations that the configurational entropy is close to 1 when the system falls out of equilibrium [38]. A detailed discussion of the behavior of pressure can be found in Ref. [29].

In Fig. 1, we report the jamming density for different mixtures, putting together our numerical results and experimental data from Ref. [39] and the theoretical results. Note that a single "fitting" parameter Σ_j, which is strongly constrained, allows the description of different sets of independent numerical and experimental data. The predictions of our theory are qualitatively similar to previous ones [12,13], but the quantitative agreement is much better. Interestingly, a similar qualitative behavior for the glass transition density has been predicted in [35,36]; although there is no *a priori* reason why the jamming and glass transition density should be related [23], it is reasonable to expect that they show similar trends [36].

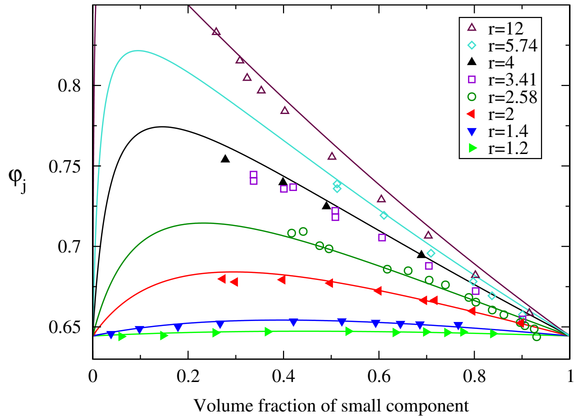

FIG. 1 (color online). Packing fraction φ_j as a function of $\eta = 1/(1 + xr^3)$ at fixed r. Filled symbols are numerical data from this work. Open symbols are experimental results from Ref. [39]. Lines are predictions from theory, obtained fixing $\Sigma_j = 1.7$. Note that the large r–small η region could not be explored, since for such very asymmetric mixtures the large spheres form a rigid structure while small spheres are able to move through the pores and are not jammed [12,13].

Finally, in Fig. 2 we report the average partial contact numbers for different mixtures. These values have been obtained by removing the rattlers from the packing. As discussed above, the total coordination is close to the isostatic value $z = 6$. This is also a nontrivial prediction of the theory (see Ref. [29]). As can be seen from Fig. 2, the computed values agree very well with the outcome of the numerical simulation, at least for r not too large. Some

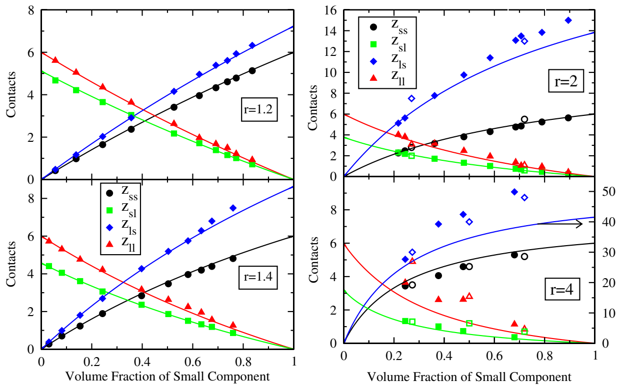

FIG. 2 (color online). Partial average coordination numbers (small-small, small-large, large-small, large-large) as a function of volume fraction of the small particles $\eta = 1/(1 + xr^3)$ for different values of r. Filled symbols are numerical data from this work. Open symbols are experimental data from Ref. [40]. Note that in the lower right panel a different scale is used for z_{ls}.

discrepancies are observed in the contacts of the large particles for large r. We produced packings of $N = 10^4$ and checked that these are not finite size effects. Also, inspection of the configurations seems to exclude the presence of phase separation. However, for these values of r and x, a large fraction of rattlers (~10%) is present within the small particles. This might affect the determination of the partial contacts. It would be interesting to check if better results are obtained using different algorithms. Experimental data from [40] are also reported in the right panel of Fig. 2.

Conclusions.—In this Letter we have extended our theory of amorphous packings to binary mixtures and have tested it against numerical and experimental data. In particular we have shown that the theory correctly predicts the variation of total density (or porosity) and local coordination with mixture composition. We have also shown that the behavior of pressure during compression follows the predictions of the theory. A striking prediction of the theory is that different compression procedures lead to different final densities, which seems to be confirmed by numerical data (see also [23,37]). Note that the only free parameter is the value of Σ_j, which is still strongly constrained (it must be close to 1). It affects slightly the values of density (by varying Σ_j in the reasonable range one can change φ_j by ~10%; see Fig. 1 in Ref. [29]) and does not affect at all the curves in Fig. 2 for the local coordinations. As stated in the introduction, we believe that these results constitute a stringent test of the idea that amorphous packings can be considered as the infinite pressure limit of metastable glassy states. Note that our results have no implications for the existence of an ideal glass transition [5,21]. Indeed, we only used numerical data obtained using fast compressions. It is possible that by using much slower compressions the physics changes dramatically and the glass transition is avoided. Still, these time scales are out of reach of current algorithms and experimental protocols.

We wish to thank A. Donev for his invaluable help in using his code, and L. Berthier for many important suggestions and for providing equilibrated configurations at high density.

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