Geometrical cluster ensemble analysis of random sphere packings

A. Wouterse[a] and A. P. Philipse
Van't Hoff Laboratory for Physical and Colloid Chemistry, Debye Institute, Utrecht University, Padualaan 8, 3584 CH Utrecht, The Netherlands

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We introduce a geometric analysis of random sphere packings based on the ensemble averaging of hard-sphere clusters generated via local rules including a nonoverlap constraint for hard spheres. Our cluster ensemble analysis matches well with computer simulations and experimental data on random hard-sphere packing with respect to volume fractions and radial distribution functions. To model loose as well as dense sphere packings various ensemble averages are investigated, obtained by varying the generation rules for clusters. Essential findings are a lower bound on volume fraction for random loose packing that is surprisingly close to the freezing volume fraction for hard spheres and, for random close packing, the observation of an unexpected split peak in the distribution of volume fractions for the local configurations. Our ensemble analysis highlights the importance of collective and global effects in random sphere packings by comparing clusters generated via local rules to random sphere packings and clusters that include collective effects. © *2006 American Institute of Physics*. [DOI: 10.1063/1.2390700]

I. INTRODUCTION

Random particle packings[1] are ubiquitous in nature and technology and can be found in divergent topics such as granular media (sand, powders), stacks of catalyst carriers, and random fibers in biological cells.[2] Despite the fact that packed particles very often have a nonspherical shape,[3,4] studies of random packings have focused on spheres.[5–8] Such studies have revealed two distinct limits of random packing, namely, random close packing (RCP) and random loose packing (RLP).

Random close packing is associated with a maximum density for a collection of randomly positioned spheres. In the extensive experiments recently performed by Aste[6] and Aste *et al.*,[7] as well as recent computer simulations,[9,10] a value of around 0.64 is found as an upper limit for the RCP sphere volume fraction, in line with earlier literature[5–8] on random sphere packings. A debated issue is whether a unique well-defined RCP density exists for this maximum random state. Torquato *et al.*[11] argued that random close packing is actually ill defined and introduced the alternative concept of a maximally random jammed state. This state refers to the largest density for which an order parameter is minimized, a criterion also used by Stachurski to define an ideal amorphous solid.[12] Another definition for RCP introduced by Roux[13] states that ideal random close packings of hard spheres are equilibrium states devoid of crystal nuclei that remain stable without friction. Compaction procedures are regarded as recipes to minimize the effects of friction. The definitions of both Torquato *et al.*[11] and Roux[13] imply the existence of a well-defined maximum density: either an order parameter has to be minimized or the constraint of no crystal nuclei has to be enforced to find the maximum random close packing density.

While random close packing refers to the density maximization of a disordered sphere packing, random loose packing is associated with minimizing the packing density to the lowest value for which a collection of randomly positioned spheres is mechanically stable in the limit of zero gravity.[8] Mechanically stable means here that the packing is in static equilibrium under a set of externally applied forces.

Solving any of the global packing problems mentioned above is quite a challenge. In this paper our primary aim is to investigate an alternative to such global extremum problems, starting from the perspective of random sphere packings composed of sphere *clusters* rather than single spheres. As typical cluster radius we choose the distance over which the pair distribution decays such that the main peaks of a distribution function from an experimental sphere packing are captured, i.e., where the distribution function starts to oscillate around 1. This approach reminds us of De Gennes's model for structural glasses where clusters of atoms or particles rather than single entities are the building blocks of a structural glass.[14]

In more detail our approach is as follows. We calculate the packing density from the frequency distribution of Voronoi volumes similar to Finney,[6,7,15] who gave an estimate for the RCP volume fraction calculated from a Voronoi analysis of experimental determined sphere configurations. Shahinpoor[16] used Voronoi volumes to construct a statistical mechanical analysis of stable random packings of granular materials where ensemble averages are obtained from a probability distribution as a function of void ratio. In this paper we combine the concept of clusters as building blocks with the statistical mechanics description from Shahinpoor to calculate ensemble averages of properties of random packing such as the probability distribution of Voronoi volumes. To obtain this distribution in our analysis a random sphere packing is considered as an ensemble of clusters of identical hard spheres, which models the constraints of nonoverlap and ran-

[a]Electronic mail: a.wouterse@chem.uu.nl

dom positioning. These clusters are generated according to well-defined local rules. Properties such as volume fraction, contact numbers, and radial distribution function are calculated as a "geometric" ensemble average over these clusters, which can be seen as the geometric equivalent of an ensemble average over phase space in the statistical mechanics of thermal systems. Generation rules for constructing sphere clusters are varied to model properties of random loose as well as close packing. First we review in Sec. II some important concepts in random packing, followed by a description of generation methods for cluster ensembles in Sec. III. In Sec. IV we discuss results from the cluster ensemble analysis and make a comparison to experimental sphere packings, in particular, the experimental data of Aste,[6] who seems to have analyzed the largest number of spheres so far.

II. PRELIMINARY

The essential approximation underlying our cluster ensemble analysis is that any sphere and its neighboring spheres in a random packing form a local configuration that is statistically independent from the other sphere configurations. This approximation enables us to use a mathematically well-defined criterion for generating geometric local cluster configurations with corresponding ensemble averages of, for example, the packing fraction. The ensemble averages are compared to values obtained from experimental and simulated random packings. Using local rules only allows us to assess any influence of global and collective effects on the properties of a random packing.

The rules for generating a cluster should produce sphere configurations that mimic the local structure in a random packing. In a stable random packing the majority of spheres are arrested at their position, whereas a minority of about 1%–3% of spheres can rattle[17] when the whole packing is shaken. The generated clusters must also have most of the spheres arrested. Donev *et al.*[18] distinguished three types of jamming for packed spheres, namely, spheres that are locally jammed, collectively jammed, or strictly jammed. A sphere is locally jammed if it cannot translate when the positions of all other spheres in the packing are fixed. Collectively jammed and strictly jammed are more stringent conditions[18] where a collection of spheres or all spheres cannot translate or rotate. Peters *et al.*[19] analyzed a specific case of local jamming, namely, the caging of a sphere with the corresponding caging number defined as the average *minimum* number of spheres that needs to be placed at random on the surface of sphere S to block all translational degrees of freedom of S with the condition of nonoverlap for spheres.[19,20] In a disorded sphere packing it is expected that as a first approximation the contacts on each sphere are distributed randomly over the sphere surface, constrained by the nonoverlap condition. Thus in our approach, for spheres in a random packing to be locally jammed, the average number of contacts at least equals the caging number if contacts are distributed randomly on the surfaces of spheres.

The mathematical criterion for a sphere S to be noncaged, namely, that a hemisphere on S can be chosen such that all contacts are part of that hemisphere,[19,20] can be cast into a problem of contact normal forces to give a more physical picture. For a noncaged sphere S all vector sums of nonzero normal forces applied at the contact points are nonzero.[21] The contact forces can only push spheres. This definition of noncaging plus the requirement that contact forces are always directed to the center sphere yields the following equation:

$$f_1\mathbf{n}_1 + f_2\mathbf{n}_2 + \ \ldots\ + f_i\mathbf{n}_i = 0 \quad \text{with } f_i \geqslant 0, \tag{1}$$

which can be written as the system of linear equations

$$\begin{aligned} &f_1\mathbf{n}_1\cdot\mathbf{n}_1 + f_2\mathbf{n}_2\cdot\mathbf{n}_1 + \ \ldots\ + f_i\mathbf{n}_i\cdot\mathbf{n}_1 = 0,\\ &f_1\mathbf{n}_1\cdot\mathbf{n}_2 + f_2\mathbf{n}_2\cdot\mathbf{n}_2 + \ \ldots\ + f_i\mathbf{n}_i\cdot\mathbf{n}_2 = 0,\\ &\ldots\\ &f_1\mathbf{n}_1\cdot\mathbf{n}_i + f_2\mathbf{n}_2\cdot\mathbf{n}_i + \ \ldots\ + f_i\mathbf{n}_i\cdot\mathbf{n}_i = 0 \end{aligned} \tag{2}$$

or

$$A\mathbf{f} = 0 \quad \text{with } \mathbf{f} \geqslant 0. \tag{3}$$

Here A is an $n\times n$ matrix whose elements are the dot products of the normal vectors n_i and f is a vector which contains the force magnitude of the ith contact with normal n_i. The trivial solution to this system of equations is $\mathbf{f}=\mathbf{0}$. If a nontrivial solution exists then a sphere is caged and the relative acceleration of two spheres at each contact point can be made zero under the application of a set of nonzero contact forces. In a static packing each local configuration has to satisfy (1) with the exception of rattlers.

In addition to contact forces from other spheres, particles in an experimental random packing may also be affected by the container wall. Spheres in a box might crystallize since the face centered cubic (fcc) or hexagonal close packed (hcp) lattice minimizes gravitational potential energy. However, when spheres in a box are quenched fast enough a stable disordered state is formed. There are several examples of sphere packings being tapped and shaken yet they stay disordered and do not settle into an fcc or hcp lattice.[22] In the present work sphere cluster ensembles are generated in unbounded space, which is convenient because it allows us to study random packing without influence of a wall in the bulk of a random packing. Having described the criteria a cluster has to satisfy, we will now outline the various methods for generating clusters with specific packing properties.

III. METHODS

We have investigated three types of algorithms to generate configurations based on a local rule to which we refer to, respectively, as the caging method, the parking method and the drop and roll method. For comparison, an additional algorithm was developed for taking collective effects into account, namely, a modification of the mechanical contraction method.[4,17] The cluster ensemble analysis for the different

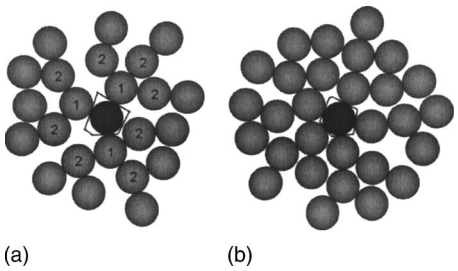

FIG. 1. Examples of two-dimensional (2D) clusters generated. The volume fraction follows from the area of the center disk divided by the area of its Voronoi cell. Shells 1 and 2 are denoted with their respective numbers. Both clusters show a stringlike structure. (a) Typical cluster generated with caging method. (b) The parking method cluster has a higher volume fraction than the caging cluster.

algorithms is compared to computer simulations of random packing in a box with periodic boundary conditions and to experimental disordered sphere packing.

A. Caging method

The caging method starts with placing a central sphere S at the origin. Neighboring spheres are subsequently added to S at random fixed positions until S is caged according to the definition in Sec. II. The added neighbor spheres in the first coordination shell are in turn caged by adding more spheres at random that yield the second shell. After the second shell, a third shell is created in the same manner. Figure 1(a) illustrates the model in two dimensions, and Fig. 2(a) shows a three-dimensional example.

B. Parking method

The parking method is very similar to the caging method except that it is based on the parking number[23] defined as the average maximum number of spheres that can be placed at random on a single sphere including a nonoverlap condition. Now a first shell of neighboring spheres is formed by adding spheres at random fixed positions on a central sphere until it is no longer possible to park more spheres. The added neighbor spheres form again the first shell. Note that owing to the definition of the parking number the central sphere will always be caged. The spheres from the first shell then form the basis for the second shell. A second shell is formed by randomly parking the maximum number of fixed spheres on the first shell, a procedure which can be repeated for additional shells [Figs. 1(b) and 2(b)].

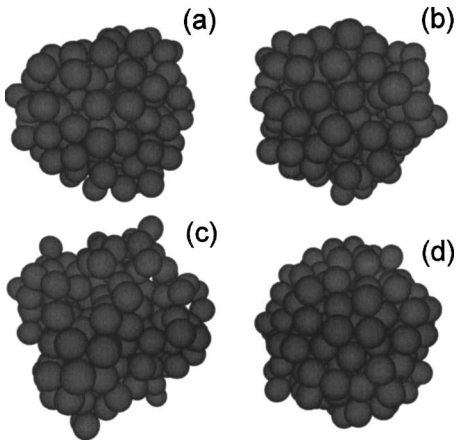

FIG. 2. Graphical representations of the generated clusters. The volume fraction increases in each picture. (a) Example of a cluster from caging method. (b) The parking method. (c) Drop and roll method. (d) Mechanical contraction method.

C. Drop and roll method

Our third method is a "drop and roll" model inspired by Ref. 24. The first coordination shell is created just as in the parking model, but the next shells are formed by a drop and roll mechanism, i.e., a sphere is dropped on the cluster from a random direction and then rolled over the cluster surface until it contacts at least three other spheres. This is repeated for a fixed number of spheres [Fig. 2(c)].

D. Mechanical contraction method for clusters

The fourth procedure is a modified version of the mechanical contraction method for spheres.[4,17] For a convenient comparison with the previous three local methods a central sphere S is held fixed at the origin around which a gas of spheres is generated. The largest distance from a sphere center to the origin defines the radius of a bounding sphere that comprises all sphere centers. The volume of the bounding sphere is reduced and the spheres are moved towards S by scaling their position. Overlap between the spheres is removed as described elsewhere for the mechanical contraction method (MCM).[4]

When the volume of the bounding sphere is minimized, the enclosed spheres start to crystallize to fit inside the bounding sphere since the most efficient packing in filling space is the fcc or hcp packing.[25] To prevent global crystallization in the container any overlap between spheres and the bounding sphere is not removed. Local crystallinity is monitored by local bond order parameters and contact numbers. As the bounding sphere shrinks, the volume fraction will at some point exceed 0.64 and a new bounding sphere is calculated. The above steps are repeated until a termination condition is met, namely, when the newly calculated bounding sphere is larger then the previously calculated bounding sphere. At the termination point the cluster will dilate because spheres have to move outwards to remove the overlap caused by scaling their position and then the bounding radius increases. This algorithm models collective effects from the presence of other spheres, in contrast to the previous three local models involving only the positioning of a single sphere per step. A typical example of a cluster is shown in Fig. 2(d).

E. Computing average properties of a cluster ensemble

For comparison to the volume fractions of a random sphere packing we calculate the ensemble average of the local cluster volume fraction. The latter is calculated employing a Voronoi cell, i.e., the region of space closer to a

TABLE I. Ensemble averages for the four cluster algorithms.

	N^a	N_c	N_1	N_2	Phi	Phi c	Phi 1	Phi 2
Cage method	3.54	4.711	4.593	3.3105	0.495	0.497	0.502	0.494
Park method	3.59	8.392	4.42	3.186	0.528	0.625	0.551	0.519
Drop and roll	7.442	8.38	6.618	7.623	0.603	0.650	0.616	0.599
MCM cluster	6.341	6.274	6.333	6.344	0.645	0.633	0.641	0.646
MCM packing	5.8				0.62			

[a]N is the average contact number of the first two shells. N_c, N_1, and N_2 are the average contact numbers, for the central sphere, the first shell, and the second shell, respectively. Phi is the average volume fraction of the first two shells. Phi c, Phi 1, and Phi 2 are the averages of the local volume fraction for the central sphere, the first shell, and second shell, respectively.

specific point than other points in the same point set. The volume of the Voronoi cell is the volume closest to the center of a sphere and the local volume fraction is obtained by dividing the volume of a sphere by its Voronoi volume[6,15,26] (see Fig. 1). Contact numbers and the radial distribution function for the central sphere are also calculated by averaging over the ensemble of clusters. The calculated ensemble averages have an uncertainty because, to form a sphere packing, clusters are merged together and it is not clear how exactly the merging of clusters will influence the calculated averages.

Furthermore, the Q_4 and Q_6 orientational bond order parameters[27] were calculated to compare the orientational order with experimental data from.[6] Q_4 and Q_6 are calculated by considering the local bonds connecting a sphere to its neighbors from the Voronoi diagram in stead of the neighbors within a fixed distance.[6] Q_l is defined as:

$$Q_l = \sqrt{\frac{4\pi}{2l+1}\sum_{m=-l}^{l} |\langle Y_{l,m}(\theta(\mathbf{r}_i), \phi(\mathbf{r}))\rangle|^2}, \quad (4)$$

where the angular brackets $\langle\ \rangle$ denote the average over the local bonds i consisting of the vectors connecting a sphere with its neighbors.

F. Modified mechanical contraction method

The properties of the clusters are also compared to random sphere packings generated by the MCM. Here a slightly different method is used: instead of contracting a system of spheres, the radii of the spheres are increased which has the same effect. In the original MCM sphere positions are scaled by a factor depending on the volume of the simulation box. This volume dependence is removed by keeping the simulation box fixed, and instead the radius of the spheres is in-

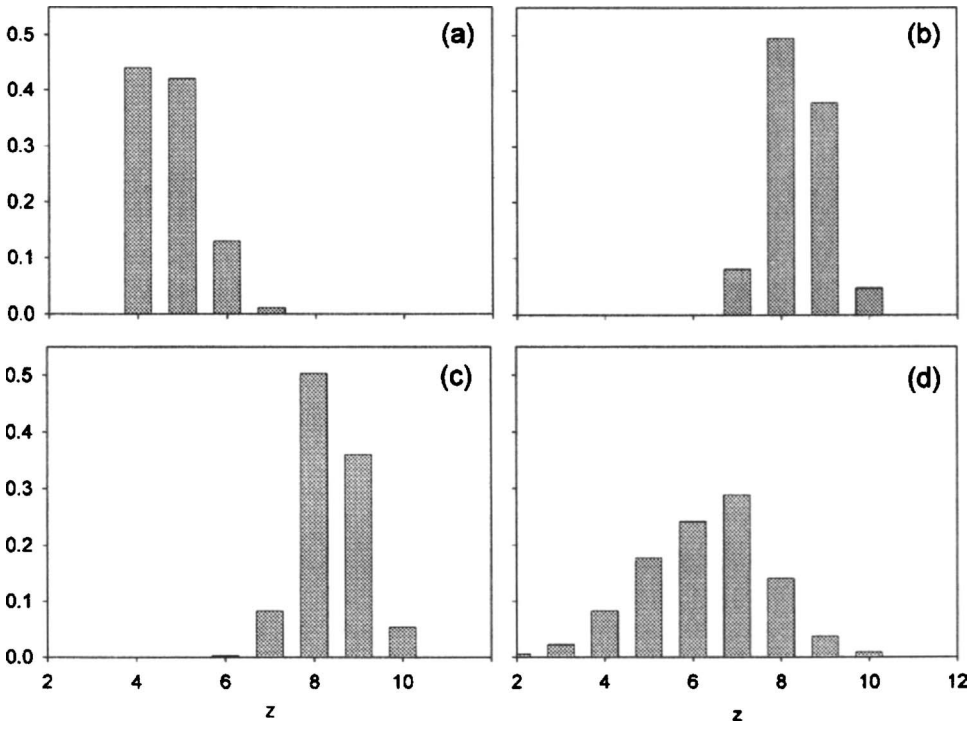

FIG. 3. Distribution of contact numbers for central sphere. (a) Caging method. (b) Parking method. (c) Drop and roll method. (d) Cluster MCM method.

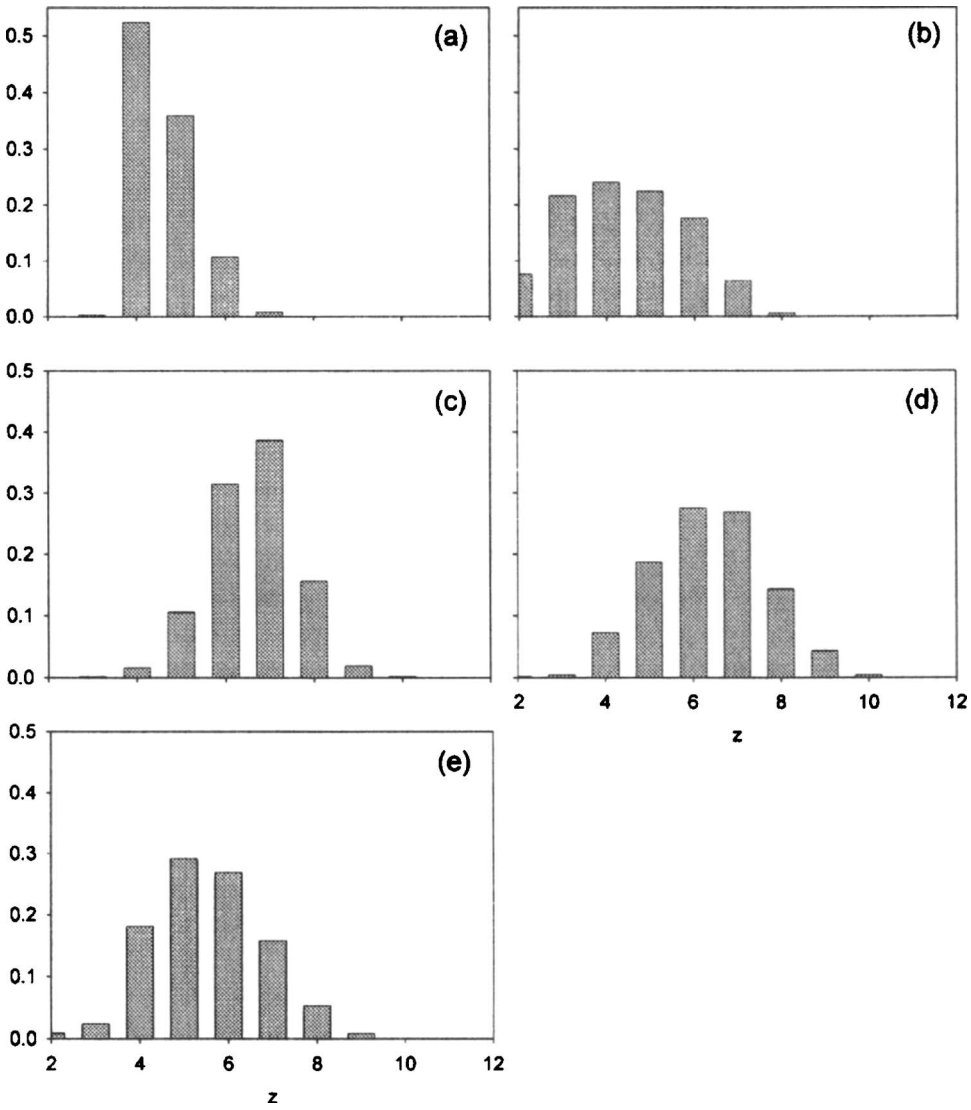

FIG. 4. Distribution of contact numbers for spheres in the first shell. (a) Caging method. (b) Parking method. (c) Drop and roll method. (d) MCM cluster method. (e) Distribution of contact numbers for spheres in a MCM packing.

creased similar to the Lubachevsky-Stillinger algorithm.[28] Overlapping spheres are separated employing the same overlap removal scheme as in MCM. As the spheres grow in size it becomes impossible at a certain point to remove the overlap. Then the volume of the simulation box is increased and the mentioned steps are repeated a fixed number of times. In the next section the results for the various algorithms discussed are evaluated.

IV. RESULTS AND DISCUSSION

The geometric ensemble averages over 1000 clusters for the four algorithms from Sec. III are listed in Table I. It should be noted that the averages over the total cluster must be treated with care since it is not known how to combine the clusters into a packing. Part of the outer shells can be shared which modifies the global average. A visualization of a typical cluster generated by each algorithm is shown in Fig. 2. The distribution in contact numbers for the center sphere and the first shell is plotted in Figs. 3 and 4. The distribution of local volume fractions for the center sphere and first shell are given in Figs. 5 and 6. The normalized radial distribution function (rdf) for the central sphere was calculated and averaged over all generated clusters in the ensemble (see Fig. 7). For all methods the rdf has a first peak at one diameter, corresponding to spheres in contact with the central sphere. For the caging method the rdf shows almost no structure after the first two peaks and the second peak is not split in two, in contrast to the other methods that yield a split second peak and a broad peak for r less than three sphere diameters. The first peak of the split peak is due to the tetrahedral arrangement of the spheres, which is absent in the caging method. The alignment of three spheres in a row produces the second peak. In Fig. 8, the Q_4 and Q_6 for a cluster ensemble are plotted as pairs and compared with the Q's calculated for a perfect crystal structure, namely, the fcc, body centered cubic (bcc), hcp, and icosahedral arrangement. The four cluster algorithms show a distribution of Q_4-Q_6 pairs, where the majority of pairs are different from the Q_4-Q_6 pairs for the crystal structures which show that the generated clusters are indeed random structures. Similar to what is reported by Aste[6] there is no icosahedral ordering present in the clusters or in the sphere packings [Figs. 8(e) and 8(f)].

A. Caging results

For the caging method we find the same caging number of 4.71, reported earlier[20] as contact number for the center

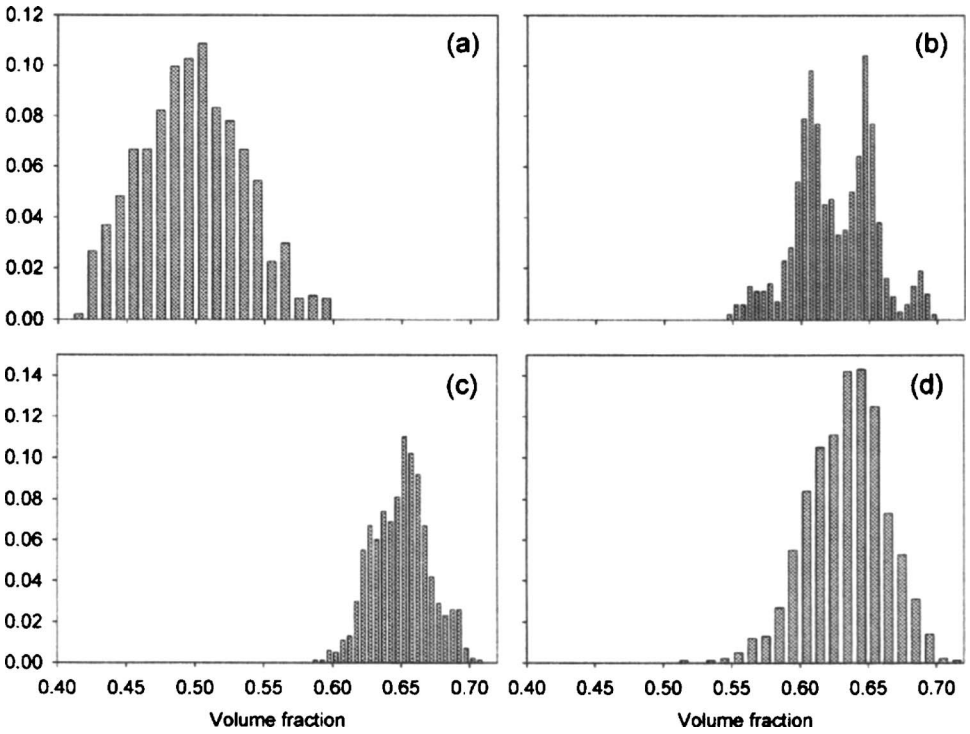

FIG. 5. Distribution of local volume fraction for central sphere. (a) Caging method. (b) Parking method. (c) Drop and roll method. (d) MCM cluster method.

sphere. In the next two shells the contact number is lower than the caging number. The volume fractions found with the caging method are surprisingly close to the freezing volume fraction of 0.495 of hard spheres and are roughly constant through all shells. The similarity between the freezing volume fraction and caging volume fraction can be tentatively explained as follows. Spheres in a fluid are immobilized due to geometric restrictions when a system of hard spheres starts to freeze upon increasing the density. Spheres in the caging cluster ensemble represent a static snapshot of such a disordered immobilized state. The freezing of hard spheres, of course, is a thermal process so when the motion of spheres is blocked, either the internal energy of the spheres needs to increase or the structure of the system needs to change. Since freezing occurs at constant temperature this means that the structure must change. The caging cluster method generates disordered structures in which spheres cannot translate and thus indeed might represent a density at which freezing occurs. This explanation, it should be noted, is clearly tentative since freezing is a dynamic process whereas caging in our definition is a pure geometrical concept.

The volume fraction of a caging cluster ensemble is compared with experimental data on random sphere packings by extrapolating a plot (see Fig. 9) of volume fraction versus contact number from Aste.[6] A best linear fit of the data was made without imposing the constraint that the fit has to intersect $z=4$ at volume fraction 0.55. For the local caging number of 4.71 a volume fraction of 0.54 is found. With the constraint the fit gives a volume fraction of 0.57. The caging volume fraction of 0.495 is lower than the random loose packing volume fraction of 0.55 found by Onoda and Liniger.[8] It makes sense that for a *global* configuration of spheres a higher volume fraction is necessary to achieve a stable packing and this is also illustrated by the two-dimensional example [Fig. 1(a)]. It is clear from the picture that a slight stress may further compact the two-dimensional cluster to make it more stable.

Silbert *et al.*[9] performed molecular dynamics simulations on frictionless and frictional sphere packings and found that the contact number of the packings depends on the friction coefficient and the coefficient of restitution of the spheres. In the limit of infinite friction the contact number asymptotes to the minimum value of 4. The contact numbers[9] for packings with a reasonably small friction coefficient are around the caging number. The low friction coefficient allows the spheres to slip and for the spheres to be jammed the force in the normal direction is more important. To balance normal forces with randomly positioned contacts a contact number close to the caging number is needed. For a contact number of 4.69, that is, very close to the caging number, the volume fraction in packings generated by Silbert *et al.*[9] is 0.59, which in turn is close to the volume fraction of 0.601 in Aste[6] where a sphere cannot move without displacing its first neighbors.

B. Parking results

For the parking method we find a reproducible, average contact number of 8.39, which is lower than the parking number of 8.7 reported in Ref. 23. For the next shell a value of 4.42 is found. Interestingly, it is not possible to achieve a value close to the parking number for the neighboring spheres. Thus by maximizing the contact number for sphere S_1, the contact number for a touching sphere S_2 is lowered because the already parked spheres on S_1 exclude volume for new spheres to be parked on S_2. In the second shell the contact number decreases further. For the parking method the volume fraction of 0.625 for the central sphere is close to the random close packing density commonly found in experimental packings of 0.62–0.64, but for shells surrounding the

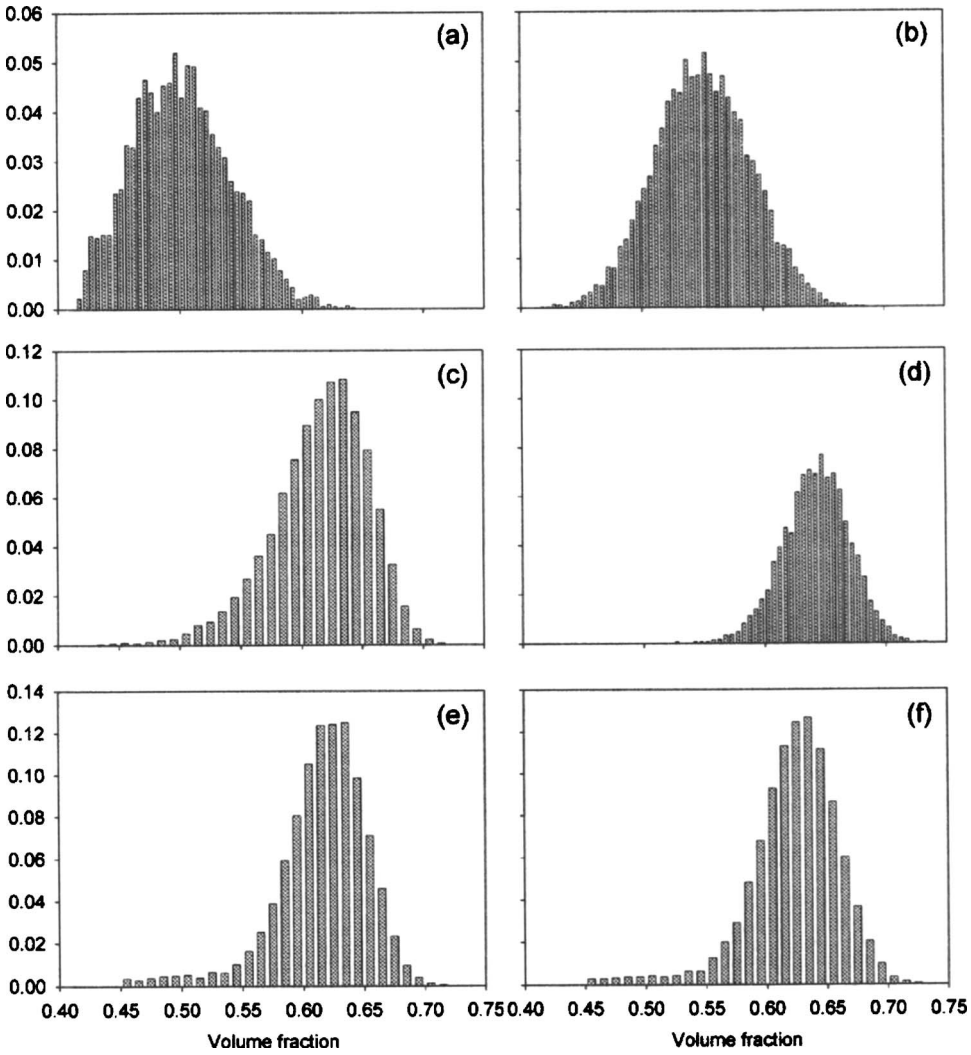

FIG. 6. Distribution of local volume fraction for central sphere and for spheres in the first shell. (a) Caging method. (b) Parking method. (c) Drop and roll method. (d) MCM cluster method. (e) Distribution of local volume fraction for spheres in a MCM packing. (f) Distribution of local volume fraction in an experimental random packing of hard spheres.

central sphere this is no longer the case due to the mentioned excluded volume effects. The cluster dilutes as it grows via parking more spheres. The already parked spheres influence the placement of new spheres and this promotes the growth of a stringlike structure, as shown in Fig. 1(b) for two dimensions. The parking model describes the structure of a random packing reasonably well as can be seen from the radial distribution functions in Fig. 7, but the overall density of 0.53 is still roughly 20% below the RCP density of 0.64.

Another interesting feature is present in the distribution of volume fractions for the central particle where a split peak can be seen [Fig. 5(b)] with one peak at 0.60 and one peak at 0.64. The origin of the split peak in the distribution is not precisely clear, but apparently there is a preference for some particular configurations due to the excluded volume effects from the nonoverlap condition. Figure 3(b) suggests a relation between the contact number and the peaks in the volume fraction distribution where the two main peaks could correspond to spheres with contact numbers of 8 and 9. The analysis of the contact number for spheres with volume fraction in the first peak ranging from 0.595 to 0.625 and 0.625–0.665 in the second peak confirms that 98% of spheres in the first peak have a contact number of 8 and 86% of spheres have a contact number of 9 in the second peak. The distribution for the central sphere supports the experimental observation that shaking and tapping a container of a random packing of spheres densifies the packing. Tapping apparently changes the ratio of 0.60 and 0.64 structures in a disordered sphere packing by increasing the average contact number.

C. Drop and roll method

For the drop and roll method the average number of neighbor spheres on the center sphere is the parking number as expected. For the next shell the number of contacts per sphere decreases to 6.62, and for the second shell the contact number is 7.62. The contact numbers are higher than those for the parking method because the drop and roll method prevents the stringlike structure as in the cluster method since the spheres are rolled until they touch at least three other spheres. The result is a higher volume fraction for the central sphere and for the surrounding shells than the parking method. The volume fraction decreases with shell number because as spheres are dropped from a random direction, the probability of hitting a sphere from a certain direction becomes nonuniform, which results in an anisotropic structure [Fig. 2(c)]. However, the contact numbers for these clusters are higher than the numbers found in random packing. Furthermore, some spheres have 12 neighbors, though there are only a small percentage as can be seen from the Q_4–Q_6

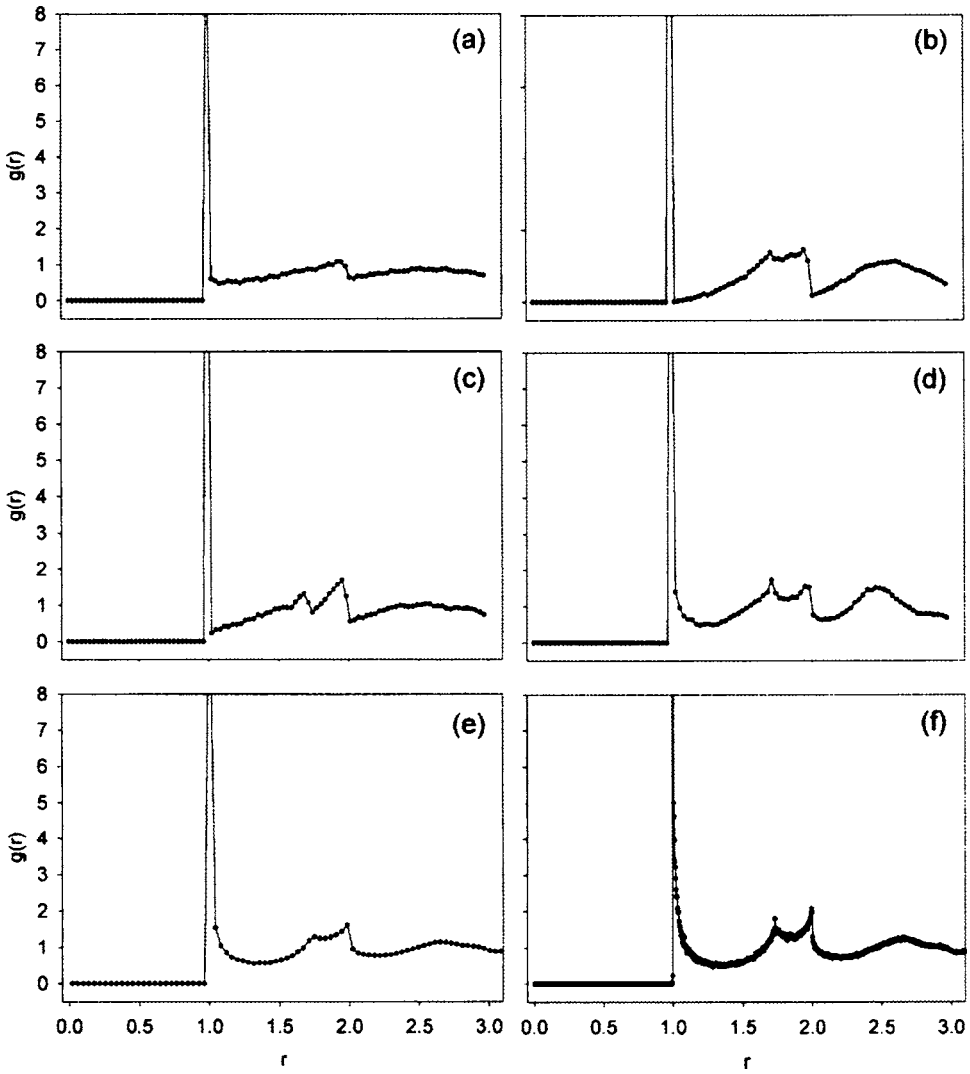

FIG. 7. Radial distribution functions for the center sphere. (a) Caging method. (b) Parking method. (c) Drop and roll method. (d) MCM cluster method. (e) MCM random packing. (f) Experimental random packing of hard spheres.

graph [Fig. 8(c)]. The rdf shows a clear split peak which is the result of rolling spheres until there are three contacts. This promotes the formation of tetrahedral arrangements.

D. MCM cluster method

For the MCM cluster method the contact number is roughly constant for each sphere shell with a value of 6.3. The MCM cluster method models the features of a random close packing better than the two other methods. The rdf matches reasonably with the rdfs for the MCM and experimental packing. The peaks in the rdf occur at roughly the same position but the shape of the peaks differs. The contact number for the central sphere is larger in the parking method than for the MCM clusters. However, the volume fraction of the center sphere is higher in the MCM model and also denser in the next shells than in the case of the parking method. The average volume fraction of 0.645 is close to the random close packing volume fraction usually cited to be around 0.64. Maximizing the coordination number locally as is done in the parking method does not maximize the overall volume fraction of the cluster. The MCM cluster method clearly shows the importance of collective effects occurring due to the geometric constraints on the spheres. By lowering the contact number for the central sphere, the first and second shell can pack more densely compared to the parking method. The collective movement of the spheres creates a more isotropic structure than for the drop and roll method. The local models only mimic the behavior of a random packing reasonably well for the central sphere and its first shell. The second shell is not representative since collective effects become more important. There are no sphere configurations formed with a contact number of 12 as can be seen from Figs. 3(d) and 4(d). From the bond order parameters [Fig. 8(d)] it can be seen that the majority of local configurations of the MCM are different than those for a fcc or hcp crystal.

E. Modified MCM for random sphere packing

The modified MCM method is an iterative volume fraction maximization procedure. The volume of the simulation box is increased at each step and spheres can reorganize themselves more efficiently. The volume fraction increases as the spheres grow in size. After a fixed number of steps the volume fraction reaches a plateau at 0.637 (see Fig. 10). The plateau of 0.637 indicates that the packing is trapped in a local volume minimum.

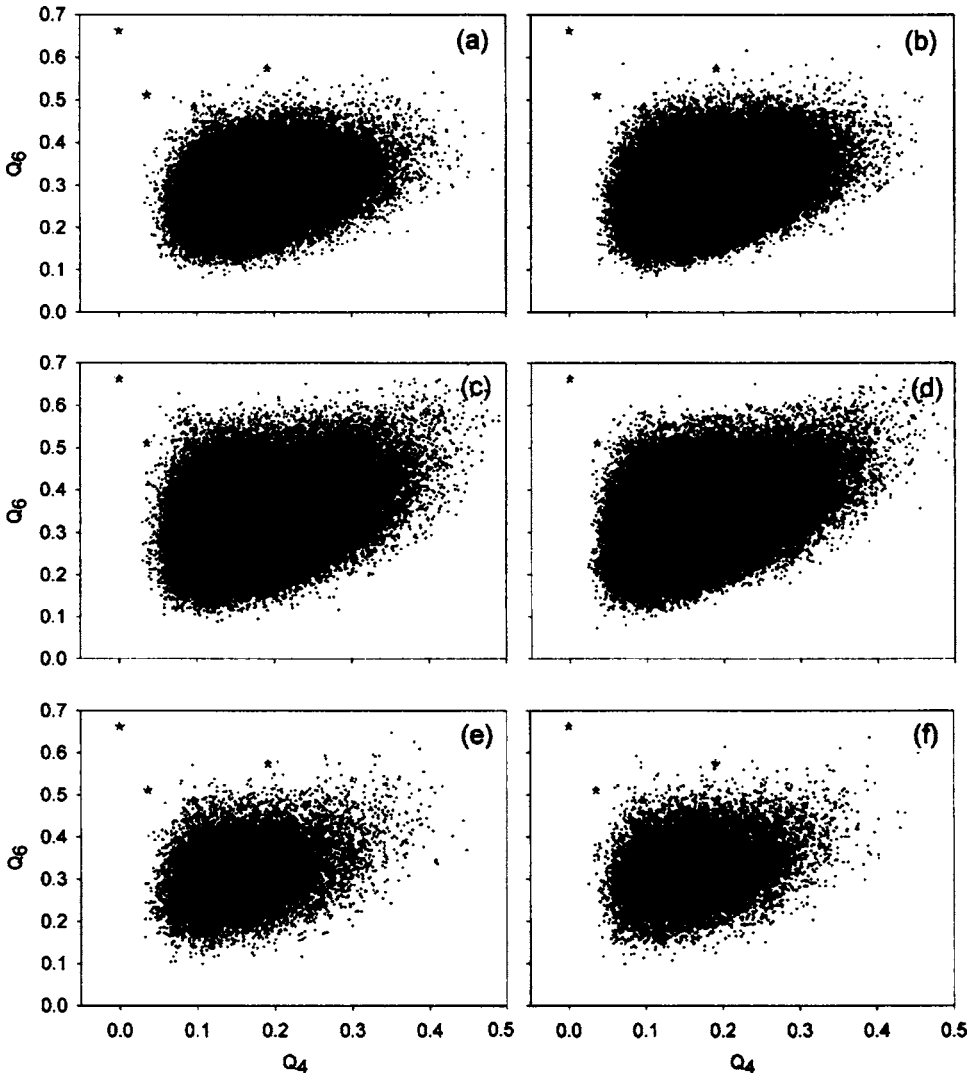

FIG. 8. Q_4 and Q_6 orientational bond order parameters. The stars represent Q_4 and Q_6 in fcc, hcp, bcc, and icosahedral. (a) Caging method. (b) Parking method. (c) Drop and roll method. (d) MCM cluster method. (e) MCM random packing. (f) Experimental random packing of hard spheres.

V. CONCLUSIONS

The cluster ensemble analysis turns out to be a versatile method in investigating properties of random sphere packings. The ensemble averages yield a lower bound for the random loose packing (RLP) volume fraction and show quantitative agreement for random close packed (RCP) volume fraction, contact numbers, and radial distribution functions. Furthermore, the ensemble analysis is useful to at least qualitatively understand the origin of RLP and RCP from a simple local geometrical analysis based on the physics of the packing formation.

The caging cluster method yields a volume fraction of 0.495, remarkably close to the hard sphere freezing volume fraction, providing a lower bound on volume fraction for

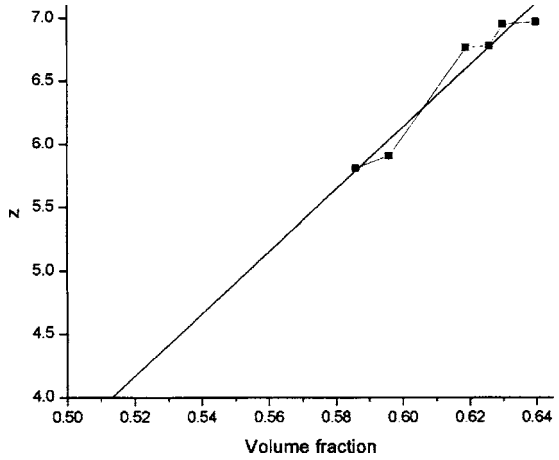

FIG. 9. Linear fit through the experimental data from Aste. Extrapolating the data yields for the caging number of 4.71 a volume fraction of 0.54.

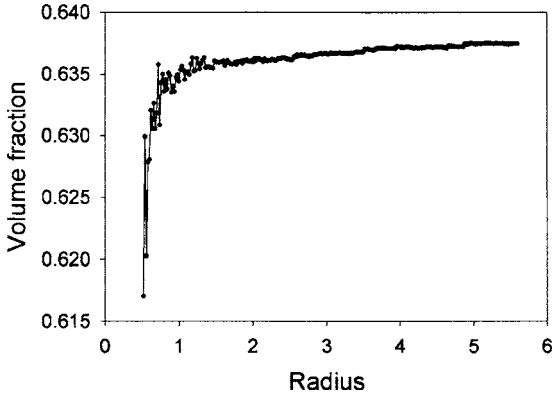

FIG. 10. Volume fraction as a function of particle radius for the modified mechanical contraction method.

random loose packing. An unexpected split peak is found in the distribution in volume fractions for the parking method, related to the contact number of the center sphere. We show that local models provide insight into the properties of random packing of equally sized spheres. Calculated radial distribution functions for the clusters show the same peaks as experimental data and computer simulations. A local orientational bond order analysis confirms that the generated clusters are indeed disordered. The radial distribution function for the parking cluster resembles the radial distribution of a random packing better than the drop and roll model where the two peaks in the rdf are clearly split. The radial distribution function of the MCM cluster method agrees with the rdf for a MCM packing and experimental sphere packings in features, but the height and width slightly differs.

The parking cluster method and the drop and roll method both generate configurations with properties similar to random close packing. These methods show that by increasing the contact number the local volume fraction increases. However, there are still some differences in properties with respect to experimental packings due to collective and global effects. The MCM cluster method remedies these effects and models a random close packing more closely since it accounts for collective effects. The MCM cluster is denser than the clusters from the local methods, and a maximization of the volume fraction is realized. For a more detailed description of random packing more complicated models are needed, which model collective effects in the generation of clusters or packings.

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[1] T. Aste and D. Weaire, *The Pursuit of Perfect Packing* (IOP, Bristol, 2000); D. J. Cumberland and R. J. Crawford, *The Packing of Particles* (Elsevier, Amsterdam, 1987).
[2] L. Miao, O. Vanderlinde, J. Liu, R. P. Grant, A. Wouterse, A. P. Philipse, M. Stewart, and T. M. Roberts (unpublished).
[3] A. P. Philipse, A. Nechifor, and C. Patmamanoharan, Langmuir **10** (12), 4451 (1994); A. P. Philipse, *ibid.* **12** (5), 1127 (1996); Corrigendum Langmuir **12**, 5971 (1996).
[4] S. R. Williams and A. P. Philipse, Phys. Rev. E **67**, 051301 (2003).
[5] J. D. Bernal and J. Mason, Nature (London) **188**, 910 (1960); G. D. Scott, *ibid.* **194**, 956 (1962).
[6] T. Aste, J. Phys.: Condens. Matter **17**, S2361 (2005).
[7] T. Aste, M. Saadatfar, and T. J. Senden, Phys. Rev. E **71**, 061302 (2005).
[8] G. Y. Onoda and E. G. Liniger, Phys. Rev. Lett. **64**, 2727 (1990).
[9] L. E. Silbert, D. Ertas, G. S. Grest, T. C. Halsey, and D. Levine, Phys. Rev. E **65**, 031304 (2002).
[10] A. Donev, I. Cisse, D. Sachs, E. Variano, F. H. Stillinger, R. Connelly, S. Torquato, and P. M. Chaikin, Science **303**, 990 (2004).
[11] S. Torquato, T. M. Truskett, and P. G. Debenedetti, Phys. Rev. Lett. **84**, 2064 (2000).
[12] Z. H. Stachurski, Phys. Rev. Lett. **90**, 155502 (2003).
[13] J. Roux, e-print cond-mat/0405358.
[14] P.-G. de Gennes, C. R. Phys. **3**, 1263 (2002).
[15] J. L. Finney, Proc. R. Soc. London, Ser. A **319**, 479 (1970).
[16] M. Shahinpoor, Powder Technol. **25**, 163 (1980).
[17] K. D. Kristiansen, A. Wouterse, and A. P. Philipse, Physica A **358**, 249 (2005).
[18] A. Donev, S. Torquato, F. H. Stillinger, and R. Connelly, J. Comput. Phys. **197**, 139 (2004).
[19] E. A. J. F. Peters, M. Kollmann, T. M. A. O. M. Barenbrug, and A. P. Philipse, Phys. Rev. E **63**, 021404 (2001).
[20] A. Wouterse, M. Plapp, and A. P. Philipse, J. Chem. Phys. **123**, 054507 (2005).
[21] A. P. Philipse and S. G. J. M. Kluijtmans, Physica A **274**, 516 (1999).
[22] J. B. Knight, C. G. Fandrich, C. N. Lau, H. M. Jaeger, and S. R. Nagel, Phys. Rev. E **51**, 3957 (1995); E. R. Nowak, J. B. Knight, E. Ben-Naim, H. M. Jaeger, and S. R. Nagel, *ibid.* **57**, 1971 (1998).
[23] M. L. Mansfield, L. Rakesh, and D. A. Tomalia, J. Chem. Phys. **105**, 3245 (1996).
[24] W. M. Visscher and M. Bolsterli, Nature (London) **239**, 504 (1972).
[25] T. C. Hales, Ann. Math. **162**, 1065 (2005).
[26] C. B. Barber, D. P. Dobkin, and H. T. Huhdanpaa, ACM Trans. Math. Softw. **22**, 469 (1996).
[27] P. J. Steinhardt, D. R. Nelson, and M. Ronchetti, Phys. Rev. B **28**, 784 (1983).
[28] A. R. Kansal, S. Torquato, and F. H. Stillinger, J. Chem. Phys. **117**, 8212 (2002).