Experiments on the Random Packing of Tetrahedral Dice

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Tetrahedra may be the ultimate frustrating, disordered glass forming units. Our experiments on tetrahedral dice indicate the densest (volume fraction $\phi = 0.76 \pm .02$, compared with $\phi_{\mathrm{sphere}} = 0.64$), most disordered, experimental, random packing of any set of congruent convex objects to date. Analysis of MRI scans yield translational and orientational correlation functions which decay as soon as particles do not touch, much more rapidly than the $\sim$6 diameters for sphere correlations to decay. Although there are only $6.3 \pm .5$ touching neighbors on average, face-face and edge-face contacts provide enough additional constraints, 12 ± 1.6 total, to roughly bring the structure to the isostatic limit for frictionless particles. Randomly jammed tetrahedra form a dense rigid highly uncorrelated material.

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Over the past decade there has been renewed interest in the ancient problem of dense packing of solid objects. Centuries after Kepler conjectured that the ordered face centered cubic (fcc) structure would yield the densest packing of spheres, the conjecture was proven by Hales [1,2]. Studies of granular materials have again raised the question of the density and configurations of random packings of spheres and other objects [3–6]. More recently, it has been shown that ellipsoids can fill space more densely than spheres in both ordered and random arrangements and the question has been raised whether it is possible to have a random packing with a higher density than a crystalline packing [7,8]. For hard particle systems the densest phase is entropically favored and is often the structure found in nature. The porosity and permeability of soil, the composition and flow of granular matter, and the density at which information can be stored all relate to packing problems which are therefore of interest in mathematics, physics, chemistry and engineering [9]. The only exact results to date are for the packing of uniform spheres in one, two and three dimensions and some limits on the minimum number of neighboring contacts for packing stability [9–12].

In this Letter we address the random packing properties of tetrahedra. Tetrahedra differ from most previously studied objects in that they have flat faces, sharp edges and vertices. The densest packing of tetrahedra is an open question, but the highest known density has risen in the past century from $\phi \sim 0.36$ to 0.72 to 0.76 to 0.78 [13–17], where ϕ is the volume fraction of space filled by the objects. The angle between adjacent faces at $\sim$70.53 degrees is highly frustrating for space filling and as we find in this letter quickly destroys both translational and orientational order making these systems interesting for glass studies. In random packings it is interesting to know the number of constraints relative to the number of degrees of freedom [10–12]. For frictionless spheres and ellipsoids, each interparticle contact corresponds to a constraint. For tetrahedra (and other polyhedra) we might expect for frictionless contacts; face-face $\Rightarrow$ 3 constraints, edge-face $\Rightarrow$ 2 constraints, edge-edge, point-face $\Rightarrow$ 1 constraint. With these assignments the 6.3 ± 0.5 contacts that we find yield 12 ± 1.6 constraints. Surprisingly, this is roughly consistent with an isostatic packing of frictionless dice with twice their 6 degrees of freedom.

The experiments were performed on a set of 1000 tetrahedral dice. A view of the top free surface of the dice in a cylinder is shown in Fig. 1(a). The surface embossed numbers correspond to less than 1% of the volume of the tetrahedra. A larger deviation comes from the rounding of the edges and corners. The side of the circumscribed tetrahedra is 2.43 ± 0.02 cm and the edges are rounded with a radius of 0.06 cm. The dice fill 0.96 of the circumscribed and 1.16 of the inscribed tetrahedra. The experiments were performed by adding dice to different size and shaped containers, shaking and adding more dice until no more could be added. For the simplest experiments the dice were added to cylinders of different radii. Packing fractions were obtained by measuring the container volumes by the weight of a known filling fluid, refilling the empty container with the dice and then weighing the fluid required to fill the packed container. For cylinders the bottom effects were first determined by measuring packing fraction vs height. The packing fraction for cylinders of different radii are shown in Fig. 1(b). The extrapolated value for a large radius container is 0.76 ± 0.02. This method was originally used for spheres by Mason and Bernal [18]. A more recent technique for minimizing the boundary effects is to fill a spherical container with the objects and then measure the volume of fluid injected from the bottom needed to fill to a certain height. Under the assumption that the particle density is spherically symmetric a cubic fit to the height vs volume curve gives the packing fraction toward the center

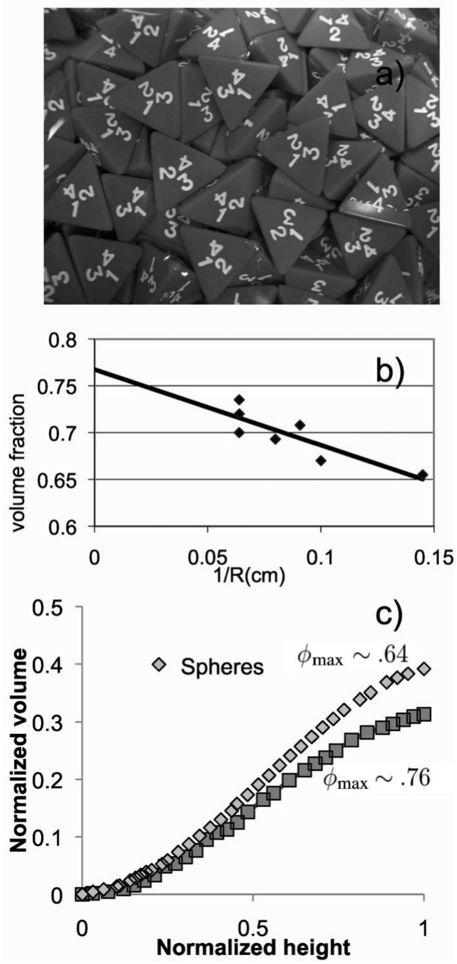

FIG. 1. (a) Tetrahedral dice used for this study; top free surface of cylindrical packing. (b) Packing fraction of tetrahedral dice in cylinders of different radii. Extrapolated value for an infinite radius cylinder is 0.76 ± 0.02. (c) Volume of water needed to fill a spherical container to a fraction of its height when packed with spheres or tetrahedral dice relative to the volume required when the container is empty of particles.

of the sphere [19]. In Fig. 1(c) we find ϕ for spheres as 0.64 ± 0.02 and ϕ for our dice as 0.76 ± 0.02. Note that the average ϕ in this spherical container is 0.61 for spheres and 0.69 for the dice.

Most of the data in this letter come from the analysis of MRI scans. In Fig. 2 we show a slice of the cylindrical sample used in these studies. The average ϕ for this sample is 0.69. The fluid surrounding the dice is water with 10 mM $CuSO_4$ added to increase T_1^{-1}. The light regions are water and the dark are plastic, enhanced by a gray scale threshold cut. Figure 2-left shows an MRI slice. Centers are found by an algorithm which fits inscribed spheres in the ‘‘dark’’ volumes, Fig. 2-middle. Another algorithm identifies orientations knowing the centers [20]. The filled regions in 2-right correspond to the fit tetrahedra. Because of the finite resolution ($0.5 \times 0.5 \times 0.5$ mm^3) of the MRI image, touching dice share common voxels. The number of contacting neighbors is determined by a number of criteria

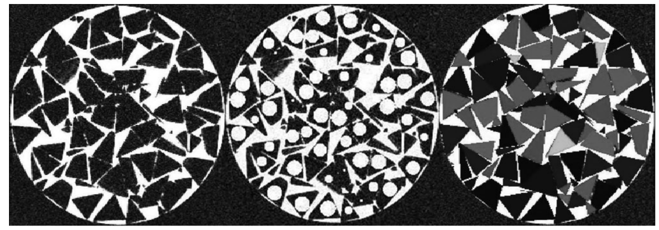

FIG. 2. Left: A slice from an MRI scan of tetrahderal dice in a cylindrical container. Water is white, dice are black. Middle: The identified inscribed spheres. Right: The dice are replaced by ideal tetrahedra with identified position and orientation.

including separation of centers and number of shared voxels. The nature of the contacts is determined by finding the dark voxels which are shared. These contact regions are then approximated as ellipsoids. The size of the ellipsoids and their aspect ratios are then used to assign a contact as point-face, edge-edge (small ellipsoid with small aspect ratio), edge-face (large prolate ellipsoid), face-face (large oblate ellipsoid), etc. Further analysis of the face and edge angles at contact refine the analysis. The position, orientation and contacts for all 311 dice not touching the container walls were found.

The radial distribution function, RDF, of the center points of the dice is shown in Fig. 3(a). In order to compare with the RDF of randomly packed spheres we normalize both curves by the minimum center-center separation. For spheres this is the sphere diameter while for tetrahedra it is $a/\sqrt{6} \sim 0.408a$ of the edge length, a, and corresponds to a closest face-face contact. There are many interesting differences between the RDF for spheres and tetrahedra (or tetrahedral dice). Since a flat RDF at $g(r) = 1$ is the result for a random point distribution the smaller departure from unity for tetrahedra suggests that the packing is ‘‘more random’’ or less correlated than random sphere packing. It is also clear from the decay in the oscillations with particle separation that the correlation length is shorter for tetrahedra than for spheres. Many of these differences can simply be attributed to the geometry of the particles; the flat face of the tetrahedra and the frustration induced by the tetrahedral angles. For spheres all contacts occur at a fixed distance, twice the radius of the sphere. For tetrahedra even face to face contacts occur over a center to center spacing ranging from $R_{\min} \sim 0.408a$ to $3R_{\min}$. For sphere packings there is both a delta function in $g(r)$ (not shown) at $r = R_{\min}$ which corresponds to the number of contacts and a divergence of $g(r)$ as $r \rightarrow R_{\min}$ due to the zero compressibility. Similarly, singularities in next neighbor spacings for spheres are lost in tetrahedra due to both the range of touching contacts and the various orientations of even face-face contacts of second neighbors.

In order to investigate angular correlations between the dice we define for the qth die the vectors $\vec{n}_{qi}$ normal to each face, $i = 1, 2, 3, 4$. For each pair of particles the function

$$S_{ql} = \Sigma_{i=1}^{4} \vec{n}_{qi} \cdot \vec{n}_{li}/4, \tag{1}$$

where i on the lth particle is chosen so as to maximize the scalar product $\vec{n}_{qi} \cdot \vec{n}_{li}$, measures whether the particles are completely superposable by translation. Completely aligned particles have $S_{ql} = 1$, the average value for randomly oriented particles is $0.74\ldots$ and the minimum value obtainable is $1/3$. The average value $\langle S_{ql} \rangle$ over all pairs in our sample is ~ 0.74. indicating no long range correlations. In Fig. 3(b) we show the correlation function $S(r) = \langle S_{ql} \delta(r - |\vec{r}_q - \vec{r}_l|) \rangle$. We see that there are very short range (anti) correlations which decay on a scale of three nearest neighbor distances, a scale similar to that of the decay of translational correlations. To see whether there are correlations between faces (independent of the rotation angle about the perpendicular to the face) we introduce

$$F_{ql} = \min(\vec{n}_{qi} \cdot \vec{n}_{lj}) \tag{2}$$

$i, j = 1, 2, 3, 4$. $F_{ql} = -1$ for face to face alignment, F_{ql} is maximum at the tetrahedral angle at $-1/3$ and for random orientation $F_{ql} = -\sqrt{3/2}$. The face-face angular correlation function $F(r) = \langle F_{ql} \delta(r - |\vec{r}_q - \vec{r}_l|) \rangle$ is shown in Fig. 3(c). Here we see that at the closest separation the faces are completely antialigned (the outward normals are antiparallel) as dictated simply by geometry. $F(r)$ decays essentially as soon as the faces can no longer overlap at a separation of $3R_{\min}$.

Previous studies of random packings, at least of spheres and ellipsoids suggest that the structures are close to isostatic, that the particles are just barely constrained, which for frictionless systems implies that the average number of touching neighbors is equal to twice the number of degrees of freedom; a coordination number Z of 6 for spheres, 10 for ellipsoids of revolution, and 12 for general ellipsoids [7]. For tetrahedra there are 6 degrees of freedom, three translational and three rotational. Of course the dice are not frictionless, but they are reasonably smooth and experiments on other systems suggest, for unknown reasons, that shaking and tapping, as in the present preparation, leads to the frictionless value. The analysis of our MRI data for the number and type of interparticle contacts is given above and is described more fully in [20] and in the supplementary material [21]. In Fig. 4 we present the histograms of our results for the fraction of dice with different types of contacting neighbors. The average number of touching neighbors is 6.3 per particle, well below the isostatic number. Interestingly more than 86% of the particles have one or more face to face contacts, and more than 95% have face-edge contacts. Not surprisingly, we find no point-point or point-edge contacts.

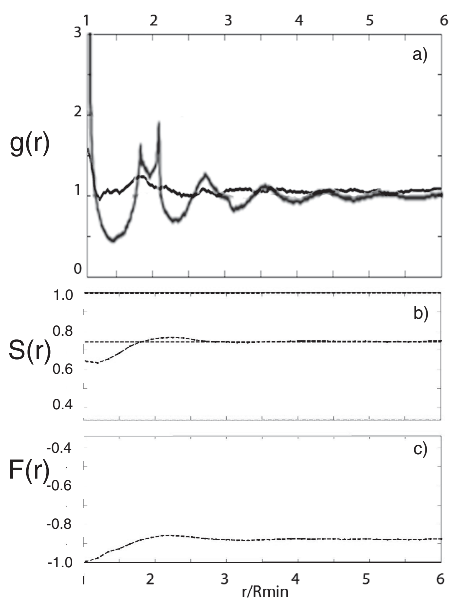

FIG. 3. (a) Radial distribution function of dice centroids compared with published results for randomly packed spheres. $R_{\min}$ is a diameter for spheres, $R_{\min} = a/\sqrt{6}$ for tetrahedra where a is an edge length. (b) Orientational correlation function for the tetrahedral dice, $S(r)$ is one for complete overlap after translation and is minimum at $1/3$. (c) Face-face correlation function, $F(r)$ is -1 for face-face contacts. All correlations decay in a distance of $\sim 3R_{\min}$ which is the furthest distance between the centers of touching tetrahedra.

Isostaticity relates to the number of constraints relative to the number of degrees of freedom [10–12]. If each contact was a constraint (and if our system were frictionless) then our system would be underconstrained and would have a large extensive fraction of "floppy" (no restoring force) modes. Previously studied systems, spheres and ellipsoids, are convex objects with no flat surfaces. Each contact is a point and when frictionless a single constraint. For both tetrahedra and for our dice there are flat faces and straight edges which contact at many (ideally infinitely many) points. However a frictionless face-face contact constrains translation perpendicular to the face and rotations about two perpendicular axes in the face. Similarly an edge-face contact constrains a translation perpendicular to the face and a rotation about an axis in the face and perpendicular to the edge. We therefore assign three constraints to each face to face contact, two to each edge to face contact and one each to edge-edge and point to face contacts. Figure 4(f) shows the distributions of constraints per particle. Here we find that the average number of constraints at 12 ± 1.6, twice the number of degrees of freedom and roughly consistent with a slight generalization of the isostatic conjecture.

Our original report of $\phi \sim 0.75$ [2,14,15] was intriguing since it was higher than the highest known crystal packing of tetrahedra at the time. Subsequently, simulations have found that tetrahedra pack randomly to better than 0.74 and the crystal packing is above 0.78 [16,17]. Since the random packing of our dice is found to be mostly face to face and face to edge we suspect that the random packing of perfect tetrahedra will be similar, certainly in the presence of very short range translational and orientational correlations.

Our experiments point to two important and related properties of tetrahedra and more generally objects with flat surfaces and edges, sharp vertices and frustrating geometries. They should be very good glass formers ther-

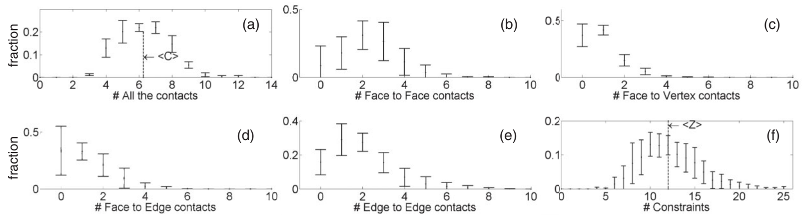

FIG. 4. Fraction of tetrahedra with specified particle-particle contacts. (a) is the total number of contacting neighbors per particle which averages to $6.3 \pm .5$. (f) is the coordination number or number of constraints per particle obtained by weighting face-face contacts by three, edge-face contacts by two, and others by one. The average coordination $\langle z \rangle$ is 12 ± 1.6. The error bars shown in the figures result from the spread of criteria used in evaluating the types of contacts.

mally and as powders they are dense, and locally rigid despite the lack of bonds or friction. (i) the random packing density is high, and may even exceed the crystal packing making crystallization less favored entropically, (ii) the translational and orientational correlations are very small so the susceptibility for crystal or liquid crystal phases is small, and (iii) the sharp vertices and face-face contacts inhibit rotation so that crystallization is kinetically hindered. Similarly rotator phases are unlikely. It appears that the geometrical frustration is more important than the high symmetry of the particles for producing such disordered structures. The existence of many face-face contacts and very short correlation lengths indicate bending rigidity on a neighbor scale about $1/3$ of a cage scale appropriate for rounded particles. This may help explain the difference in mechanical properties of rounded and angular granular matter. The concept of generalized isostaticity from number of contacts to number of constraints will be useful in other contexts.

In the time since our initial submission there has been a flurry of activity regarding tetrahedral packing [22,23]. A remarkable paper indicates that tetrahedra form a thermodynamic quasicrystalline phase at densities to $\phi \sim 0.7$. Compression of this structure gives $\phi \sim 0.83$. The latter paper and several preprints show that several different crystalline packings above 0.85 exist. The existence of many high density ordered phases leaves an interesting question as to what nature will choose thermodynamically and kinetically. A glasslike mixture is a possibility.

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