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LETTER TO THE EDITOR

Orientational order in amorphous packings of ellipses

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Abstract. We perform Monte Carlo simulations of the pouring of elliptical particles into a two-dimensional box under the influence of a uniform gravitational field. Ellipses with sufficently large aspect ratios form novel packings that we call 'nematic glasses'. The granules in these packings are ordered orientationally, and yet the packings are amorphous. A heuristic explanation of the formation of this state is presented.

In most granular media, the grains are not identical spheres. For example, sandstones are formed from particles with a variety of shapes and sizes [1]. Since sandstones are important reservoirs for oil, water and natural gas, the porosity of these packings is of great economic importance [2]. In ceramics processing and metallurgy, a wide range of materials are formed by sintering powders composed of polydisperse aspherical particles [3]. Finally, it has recently been shown that granular conducting polymers can be formed from colloidal dispersions [4–8]. In the case of polyaniline [7, 8], the polymer microparticles are prolate ellipsoids. In short, there is a wide range of technologically important granular materials in which the granules are aspherical. Despite this fact, random packings of aspherical particles have received only limited theoretical attention [9, 10].

Granular and amorphous materials have frequently been modelled using random packings of identical spheres [11–15]. Random packings formed by the pouring or settling of grains are particularly important in applications. In all likelihood, a random metastable state will result when a collection of identical spheres is poured into a container, rather than the regular 'crystalline' arrangement in which the lowest energy is achieved. This metastable state is called a loose random packing. Repeated vertical shaking of a loose random packing results in the formation of a more compact structure, a dense random packing. In three dimensions (3D), loose and dense random packings are distinct, but in two dimensions (2D) the distinction is not as clear [16]. There is also evidence that dense random packings of disks may be mechanically unstable [16]. As a result, it may be that in 2D, by applying a suitable set of perturbations a dense random packing can be reduced to a crystalline array. In contrast to the 2D case, spheres form stable dense random packings. The difference is that the 3D system exhibits frustration, while the 2D system does not. Frustration is a result of competition between local and global minimization of potential energy [17].

In this letter we present the results of the first Monte Carlo simulations of freely rotating aspherical particles poured into a container under the influence of a uniform gravitational field. Specifically, we have simulated the pouring of a collection of hard ellipses into a 2D box for a variety of different aspect ratios. In the resulting packings, the ellipses tend to have their long axes aligned with the horizontal, and the degree of orientational order is an increasing function of the aspect ratio. The

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amount of translational order present decreases with increasing aspect ratio. For sufficiently large aspect ratios, the centres of mass exhibit amorphous disorder, even though there is long-range orientational order.

In order to model granular aggregates composed of aspherical particles, we simulate the concurrent deposition of a relatively large number of 2D elliptical particles in a box. All of the particles are identical with semimajor axes of unit length and aspect ratio α. The simulation program keeps track of the centre-of-mass location of each particle, and the angle θ between the semimajor axis of each particle and the x-axis.

To simplify the simulations, we discretized the particle positions and orientations. The centres of mass are represented by points on a square lattice, while the orientations are taken from a set of uniformly spaced angles in the interval $[0, 2\pi)$. The spacings of the lattice and the angles are chosen to be small enough that the discretization does not significantly alter the properties of the final packings, but large enough that the simulations run in a reasonable amount of time [18].

Our simulation method is based on the technique introduced by Rosato *et al* in their simulations of the pouring and shaking of disks [19,20]. We begin by randomly placing N particles in a box. The size of the box is chosen so that the final packing will be roughly square and so that the average density of the initial distribution of particles is γ. Here, γ is the fraction of the total box area covered by the particles. In a real experiment, it would be difficult to arrange the particles randomly in a vertical box and then allow them to fall. A more likely scenario would be to pour particles into the top of a box at a given rate. The parameter γ can be thought of as being analogous to the rate of pouring. The walls of the box are taken to limit the motion of the centres of mass of the particles but not their orientations. The particles are randomly distributed within the volume of the box with the constraint that the centres of mass of each pair of particles must be separated by a distance of at least 1. Thus the particles cannot overlap and there are absolutely no orientational correlations at time $t = 0$.

Once the particles have been placed within the box, the pouring is simulated using the Monte Carlo method [21]. In the standard Monte Carlo algorithm, we would start by randomly choosing a particle, and then randomly choose a translation vector and an angle to rotate the particle through. Next, we would compute the change in energy and hence the probability of accepting the trial move. Since the particles are macroscopic and the temperature is taken to be comparable to room temperature, we exclude all upward movements of the particle, and accept all downward movements with equal probability [20]. In the standard algorithm, if the new position and orientation do not cause an overlap, we move the particle into the new configuration. However, if we simply move the particle to its new position and orientation, we introduce the possibility of 'jumping' over a forbidden configuration and arriving at a configuration that is allowed, but unreachable. To avoid this possibility, we instead 'propagate' the particle through the system.

To propagate the particle, we compute the angular velocity needed to place the particle in the correct final orientation when its centre of mass reaches its final position [22]. The sense of the rotation is randomly chosen. We step the particle along the trajectory, one grid point at a time, until the particle collides with another particle, collides with one of the walls, or reaches the final configuration. In the event of a collision, the particle is restored to the position it had just before the collision, and the propagation is ended. Collisions with other particles are detected using the

Vieillard-Baron criterion [23]. In all of our simulations, the maximum translation distance was taken to be three times the semimajor axis length.

We continue to move particles using the algorithm just described until the system is close to a metastable state. In a test run, we determined that the total potential energy of the system had come to within 0.7% of its asymptotic value by the 10^6th attempted move. Our subsequent simulations were all ended after the 10^6th attempted move. This sequence corresponds to pouring the particles into the box once, with no subsequent shaking.

The value of the orientational order parameter $Q \equiv N^{-1}\sum_{i=1}^{N}\cos(2\theta_i)$ indicates how much orientational order is present in a packing. Here, θ_i is the angle for the ith particle. A uniform distribution of angles will result in $Q = 0$, while if all particles lie flat, $Q = 1$. We found that Q was within 1% of its asymptotic value by the 10^6th attempted move of the test run.

Figure 1 is a representative packing for particles with aspect ratio $\alpha = 4$. A histogram of the particle populations versus angle for this packing exhibits a peak about $\theta = 0$, and so the particles are preferentially aligned with the horizontal. There are no other peaks, indicating that there are no other preferred orientations.

Figure 2 shows the orientational order parameter Q as a function of $1/N$ for $\alpha = 4$ and $\gamma = 0.25$. Although the results are somewhat noisy, there does not seem to be a significant trend. Q almost certainly does not tend to zero as $N \to \infty$.

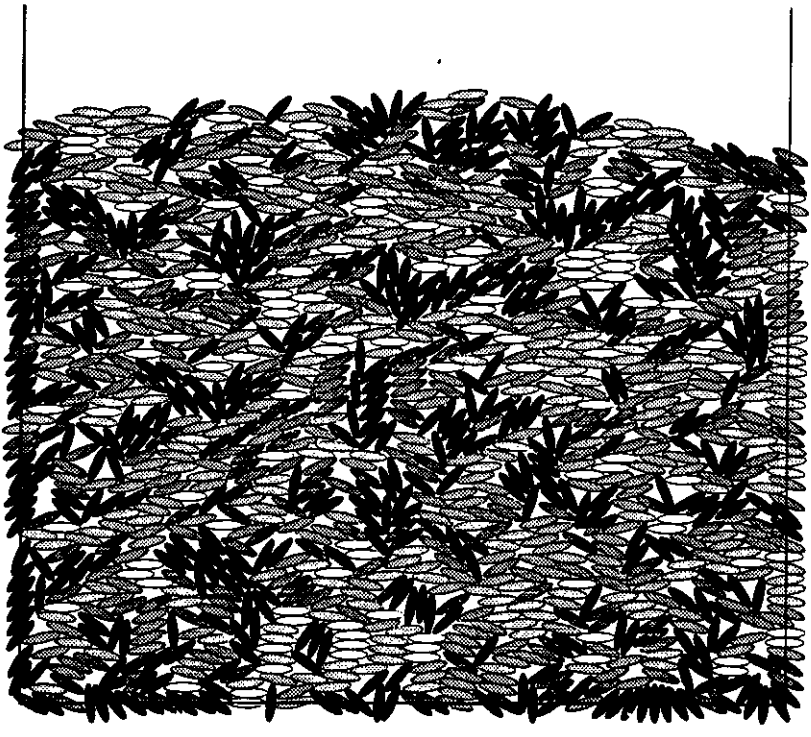

Figure 1. A packing of 1200 ellipses with aspect ratio $\alpha = 4$. The shading of each particle is proportional to $|\theta - \pi/2|$, where $\theta = \pi/2$ is represented by black and $\theta = 0$ is represented by white. The parameters for this simulation were $\gamma = 0.25$, $\alpha = 4$, and $N = 1200$.

Therefore, the non-zero value of Q we observe is not merely a finite-size effect, and we can be confident that the orientational order persists in the limit $N \to \infty$.

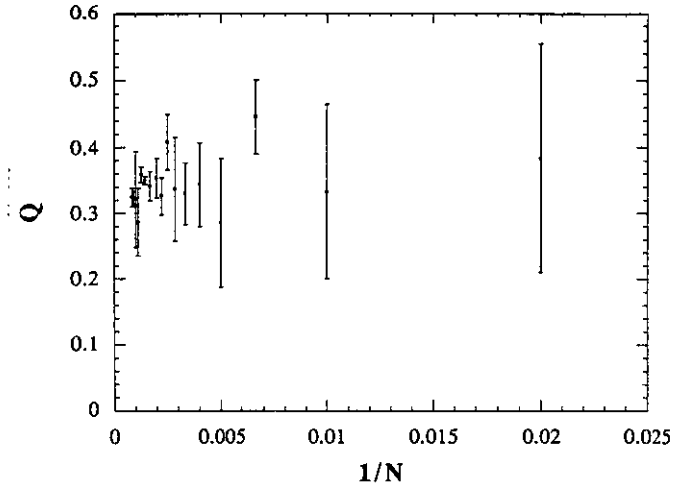

Figure 2. The orientational order parameter Q as a function of $1/N$ for $\alpha = 4$ and $\gamma = 0.25$. The points are averages over 6 simulations for $N \leqslant 800$. For $N > 800$ the points are averages over 4 simulations.

Figure 3 illustrates the dependence of Q on α. Each point in figure 3 corresponds to an average over 5 simulations with 600 particles each. Simulations were performd for $\gamma = 0.25 \pm 0.00005$ [24] and $\alpha = 32/n$, where n is an integer in the range $4, \ldots, 32$. The orientational order parameter Q increases with α. This increase is rapid at first, but saturates as α grows large. We note that $Q = 0$ for $\alpha = 1$, as expected.

It is easy to understand why Q is non-zero for $\alpha > 1$ and why it increases with increasing aspect ratio. Each particle 'wants' to minimize its gravitational potential energy. This means that each particle would 'like' to position its centre of mass as low in the box as possible. As a first approximation, assume the particles fall one at a time onto a well defined surface. Particle orientations other than horizontal incur a potential energy penalty. As we increase the aspect ratio, we increase this energy penalty and, as a result, the particles are more likely to lie flat.

We define the crystallite size to be $\Delta x \equiv 2\pi/\Delta k$, where Δk is the full width at half maximum of the first peak in the angular average of the structure factor $I(k) = (2\pi)^{-1} \int_0^{2\pi} \mathrm{d}\theta_k S(k, \theta_k)$. Figure 3 shows that Δx decreases rapidly with α. For $\alpha \lesssim 2$, the packings are polycrystalline. When $\alpha \gtrsim 2$, the crystallite size is less than the semimajor axis length, and so the packings are 'amorphous'. To be precise, for $\alpha \gtrsim 2$ the centres of the particles have no translational order. In spite of this, there is long-range orientational order in the long axes of the ellipses.

In contrast to 3D sphere packings, the lack of translational order in 2D packings of ellipses cannot be attributed to frustration. However, the reduction in the translational order with increasing aspect ratio can be readily understood. First of all, when we increase α, we decrease the energy penalty for stacking in a square lattice as compared to stacking in a close-packed triangular lattice. This means that

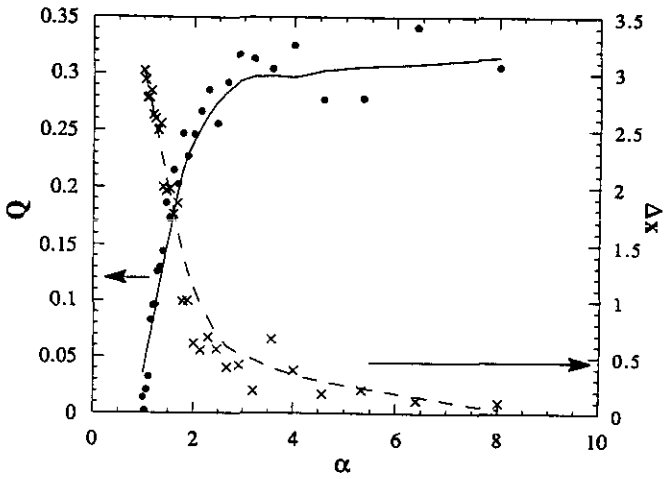

Figure 3. The orientational order parameter (full circles) and the characteristic crystallite size Δx (crosses) as a function of the aspect ratio α. Each point is the average of 5 simulations of 600 particles. The full and broken curves are guides to the eye. These simulations were run at constant initial density, $\gamma = 0.25 \pm 0.000\,05$.

the particles are more likely to form packings that are mixtures of the two different lattices. Secondly, for $\alpha > 1$, there is always some orientational disorder. For large α, small perturbations in the orientational order lead to large perturbations in translational order. The combination of these two effects quickly destroy the translational order as we increase α.

A nematic liquid crystal is a system of rod-shaped molecules in which the centres of mass are randomly distributed (as in an ordinary liquid), but the long axes of the molecules are preferentially aligned along a certain direction [25]. Our packings are 'glassy' for $\alpha \gtrsim 2$, and yet still exhibit long-range orientational order. In analogy to nematic liquid crystals, we propose to call an amorphous packing with orientational order a 'nematic glass'.

In addition to the results reported in this letter, we have examined the dependence of Q and Δx on γ. We have also studied the porosity of the the packings as a function of both α and γ. Interestingly, we find that the porosity is not a monotone function of the aspect ratio. Finally, our preliminary work indicates that shaking reduces the orientational order but does not enhance the translational order. These results will be presented elsewhere [26].

We are currently extending our work to packings of aspherical particles in 3D. Even with simple objects like ellipsoids of revolution, the additional degree of freedom introduces a number of complications. We expect different types of ordering for prolate and oblate ellipsoids. For prolate ellipsoids, the long axis of the ellipsoid will tend to align with the horizontal, but its projection onto the x–y plane will be uniformly distributed. For oblate ellipsoids, the short axes should be preferentially aligned with g. The results of a simulation of pouring ellipsoids in 3D will appear in a future publication.

In summary, pouring ellipses in a gravitational field forms a packing with a degree of orientational order. The degree of ordering grows with increasing aspect ratio. We

have also shown that the packings are polycrystalline in the $\alpha \rightarrow 1$ limit, and that the mean crystallite size swiftly decreases with increasing α. Since the aggregates are amorphous for $\alpha \gtrsim 2$, but nonetheless exhibit orientational order, we have dubbed these packings 'nematic glasses'.

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References

[1] Selley R C 1988 *Applied Sedimentology* (London: Academic) 64–5
[2] Berg R R 1986 *Reservoir Sandstones* (Englewood Cliffs, NJ: Prentice-Hall)
[3] Kuczynski G C, Uskovic D P, Palmour H III and Ristic M M 1987 *Sintering '85* (New York: Plenum)
[4] Bjorklund R B and Liedberg B 1986 *J. Chem. Soc. Chem. Commun.* 1293
[5] Armes S P and Vincent B 1987 *J. Chem. Soc. Chem. Commun.* 288
[6] Armes S P, Miller J F and Vincent B 1987 *J. Colloid Interface Sci.* **118** 410
[7] Armes S P and Aldissi M 1990 *Polymer* **31** 569
[8] Armes S P, Aldissi M, Agnew S and Gottesfeld S 1990 *Mol. Cryst. Liq. Cryst.* **190** 63
[9] Void M J 1959 *J. Phys. Chem.* **63** 1608
[10] Baxter G W and Behringer R P 1991 The flow of a collection of aspherical particles has been modelled using a cellular automaton *Physica* **51D** 465
[11] Bennett C H 1972 *J. Appl. Phys.* **43** 2727
[12] Turnbull D and Cohen M H 1964 *Nature* **203** 964
[13] Shahinpoor M 1980 *Powder Tech.* **25** 163
[14] Mehta A and Edwards S F 1989 *Physica* **157A** 1091
[15] Visscher W M and Bosterli M 1972 *Nature* **239** 504
[16] Berryman J G 1983 *Phys. Rev.* A **27** 1053
[17] Nelson D R 1983 *Phys. Rev.* B **28** 5515
[18] The semimajor axis is 32 grid units long and the orientation can take on 60 discrete values in the simulations presented here.
[19] Rosato A, Strandburg K J, Prinz F and Swendsen R H 1987 *Phys. Rev. Lett.* **58** 1038
[20] Rosato A, Strandburg K J, Prinz F and Swendsen R H 1986 *Powder Tech.* **49** 59
[21] Binder K 1986 *Monte Carlo Methods in Statistical Mechanics* 2nd edn (Berlin: Springer)
[22] Actually, there are a countably infinite number of angular velocities that will place the particle into the correct final orientation. The choices for the angular velocity are reduced to the set for which the particle will not spin in place. The angular velocity used to propagate the particle is then chosen randomly and with uniform probability from this set.
[23] Vieillard-Baron J 1972 *J. Chem. Phys.* **56** 4729
[24] The initial aerial density was not exactly 0.25 in each case because we discretized space.
[25] de Gennes P G 1974 *The Physics of Liquid Crystals* (Oxford: Clarendon)
[26] Buchalter B J and Bradley R M unpublished