# Shape-mediated ordering in granular blends

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Many industries mix granular materials of different sizes and shapes. Product quality and consistency are often compromised by demixing of constituent components. Not only is this practically problematic but it is also philosophically unsettling, for on smaller colloidal scales, systems consisting of particles differing by size and shape display quantitatively predictable transitions between mixed and separated phases. We report here that patterns and segregation transitions analogous to those seen in colloidal systems can be found in granular blends differing in shape, concentration, and temperature. This provides insights into the mechanisms of granular segregation.

Granular materials are well known for their tendency to spontaneously segregate due to differences in size, density, shape, and angle of repose. This plays a role in geophysical pattern formation [1] and can lead to processing problems in industry [2]. Pharmaceuticals in particular are constrained by tight regulatory standards [3] and are synthesized in a variety of distinct crystal morphologies whose properties affect their flow and mixing behaviors in poorly understood ways [4]. Notwithstanding their importance, understanding of mechanisms leading to segregation of simple grains is closer in many respects to an art than to a science.

By contrast, on molecular or colloidal scales, particles can exhibit sharp and predictable transitions between segregated and mixed states [5]. A key principle that governs these transitions is that of entropic ordering [6]. Entropic ordering defines conditions under which components in a mixture—typically a solvent and a solute—will either separate or mix based on which state is more probable. That is, if there are more ways of arranging the components in a separated than in a mixed state, then the system will more likely be found in the separated state. Thus a small number of plates displace a smaller volume if they are aligned and stacked together than if they are disoriented—and as a consequence, low concentrations of plates tend to be found in separated and tightly packed configurations that provide more volume for spherical solvent molecules to be arranged in multiple ways—a phenomenon known as the depletion effect [5].

The counterintuitive notion that macroscopically ordered states can actually be more probable than disordered ones is manifested in the emergence of sharp transitions as temperatures or concentrations are changed by small amounts in liquid crystals [5] or even human blood, where the formation of aggregated "rouleaux" of red blood cells has been proposed to be associated with an entropic mechanism [7]. In this Brief Report, we show that in spite of the disparity in scale, granular mixtures exhibit similar segregation transitions to those seen in polymers and colloids.

Thermodynamic arguments have been made for granular problems in the past by constructing a thermodynamic formulism for granular assemblies [8] and calculating thermodynamic equivalents of temperature and entropy for granular mixtures [9]. Recent work has demonstrated that vibrated rodlike particles form a nematic phase in a similar way to that seen in colloidal liquid crystal ordering [10]. In these systems, the ordering mechanism appears to be associated with macroscale kinetic forces between the rods rather than being due to an entropic influence. Furthermore, similarities between depletion attraction events responsible for self-assembly in colloidal systems [11] have been exposed with granular crystallization studies [12]. Parallels between colloidal systems and granular materials with respect to entropy are limited because a granular system is open and nonequilibrium; nevertheless, the resemblance between results presented here and those seen in macromolecular systems supports the possibility that a thermodynamic formulation may be useful for granular ensembles.

In analogy with approaches used for microscale mixtures, we examine here the hypothesis that ordered packings of platelike and spherical grains should occur at moderate granular temperatures and at high concentrations of spheres. To this end, we quantitatively evaluate whether ordered granular states of spheres and plates occur (1) above a critical concentration of "solvent" grains and (2) in a confined range of granular temperatures (defined shortly).

To test this hypothesis, we vibrate a shallow bed of differently shaped macroscopic grains, keeping the vibration amplitude low (under 1 mm) and the bed thickness small (less than three grain layers [13]) to suppress convective flows that could otherwise rearrange any incipient ordered states. For our purposes, the natural shapes to use for comparisons with colloidal literature are flat [5] hexagonally packing "platelets" mixed with a "solvent" of smaller spherical grains. Many common pharmaceuticals—such as acetaminophen, ibuprofen, and erythromycin [14]—are found in platelike morphologies and are plagued by segregation problems [2]. In addition, despite the large amount of granular research, there is still very little experimental research dealing with platelike particles.

In Fig. 1, we show characteristic patterns produced using platelets made from simple brass hex-nuts and a solvent of

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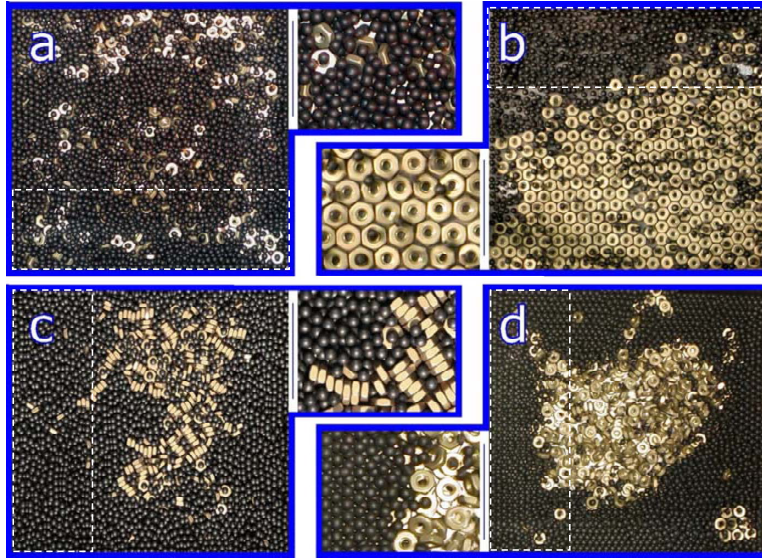
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FIG. 1. (Color online) Patterns observed in vibrated system (main plots) and enlargements (insets) of hex-nuts and spheres. (a) Mixed state vibrated at 60 Hz and $\Gamma=4$, with sphere volume fraction $\varphi=0.47$. The dimensionless acceleration is $\Gamma=A\omega^2/g$, where $A$ and $\omega$ are the amplitude and the frequency of the vibrating plate. (b) Hexagonal sheet of hex-nuts at 80 Hz, $\Gamma=2.4$, and sphere volume fraction $\varphi=0.20$. (c) Discotic state: 80 Hz, $\Gamma=2.5$, and $\varphi=0.38$. (d) Segregated state: 40 Hz, $\Gamma=2.25$, and $\varphi=0.38$. Spheres are glass beads with diameter $D=4$ mm and platelets are hex-nuts (8 mm across, 3 mm thick). The hex-nuts are brass, chosen to prevent magnetic interactions. The density ratio between the hex-nuts and the beads, once the hole in each nut is taken into account, is about 2.4:1. The volume fraction of spheres is varied by adding spheres, keeping the number of hex-nuts constant at 300. The grains are placed in an 18-cm-wide rectangular acrylic container whose walls coincide with the boundary of the snapshots and are vertically vibrated by a commercial shaker (Vibration Test Systems, Aurora, OH, model VG 100-6). The container is leveled at rest to within 0.1° as measured by digital level, and vertical accelerations are measured using a piezoelectric accelerometer (PCB Piezotronics, Depew, NY).

spherical glass beads. Three parameters are varied: the frequency ($\omega$) and dimensionless acceleration ($\Gamma$) of the shaker and the volume fraction of spheres ($\varphi$). Four types of patterns are readily distinguishable as particle volume fractions and vibration parameters are varied. In Fig. 1(a), we see a mixed state in which no apparent alignment or assembly of particles is seen. By comparison, in Fig. 1(b), we see a hexagonal packing of the flat nuts and, in Fig. 1(c), we see a state exhibiting multiple packed columns of nuts resembling the discotic or columnar state of colloids [15]. Interestingly, in Fig. 1(b), while the hex-nuts form a strongly ordered pattern, the solvent grains remain disordered. At higher accelerations, structures form and disintegrate too rapidly to remain locally hexagonal or discotic, and in this energetic state, shown in Fig. 1(d), the hex-nuts are observed to segregate from the beads and move energetically while the beads are compacted together and move at lower speeds in a nearly crystalline state. This pattern persists up to the maximum acceleration of our shaker. Under lower frequency vibrations (10–20 Hz), similar patterns to those identified at high frequencies have been observed; however, these patterns coexist with a heaping instability [16] that complicates their dynamics and so are not examined further.

A variety of ordered as well as disordered states can be seen in this model granular system. In an attempt to quantify the pattern formation, we evaluate the mean granular temperature. The temperature is defined for our granular problem to be $E=\frac{1}{2}m\langle V_f^2\rangle$, where $m$ is the mass of the particle species of interest and $\langle V_f^2\rangle$ is the mean-squared fluctuational velocity of that species [17]. We focus on the translational

motion of the particles, as the hex-nuts do not significantly rotate, so we neglect any rotational contribution to the overall fluctuational energy.

The dependence of the normalized fluctuational energy, $E$, for both spheres and hex-nuts on acceleration applied by the shaker, $\Gamma$, is shown in Fig. 2. In our nonequilibrium system it is apparent that the energies of the two species differ. At the concentration shown ($\varphi=0.38$) ordered patterns are seen only within $3\lesssim\Gamma\lesssim5$. Outside of this range, local order dis-
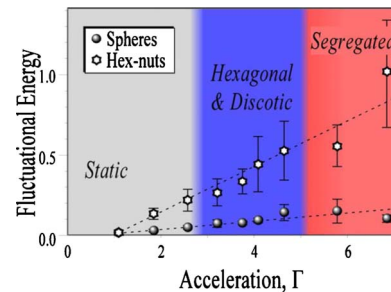


FIG. 2. (Color online) Granular fluctuational energy of the spheres and hex-nuts versus increasing dimensionless acceleration, $\Gamma$. The fluctuation velocity is normalized to the highest measured value. Regime transitions are not known precisely and are indicated midway between accelerations at which patterns are unambiguously identified. The frequency is 60 Hz, $\varphi=0.38$, and the error bars are standard deviations of three trials in which we measure grains for 0.1 s. We obtain $V_f$ by evaluating the variance of horizontal particle speeds obtained from 20 randomly selected surface particles tracked over 25 frames of high speed camera images taken at 250 frames/s (Redlake MASD, Inc., MotionScope, PCI 1000 s).
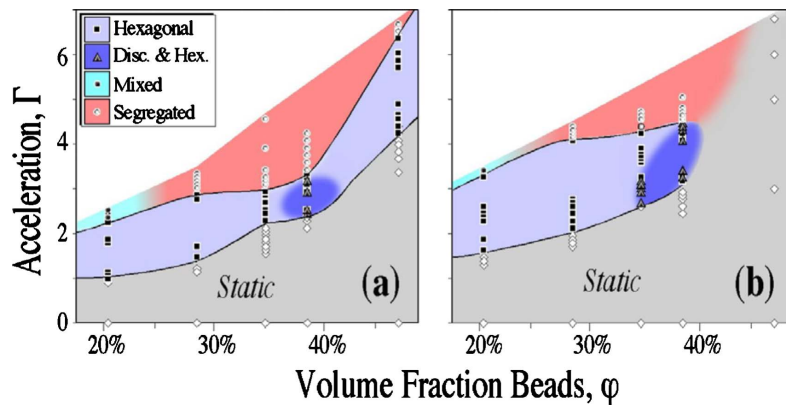
FIG. 3. (Color online) Phase diagram of ordering state versus acceleration and sphere volume fraction: (a) 60 Hz; (b) 80 Hz. Each transition point is measured at the point shown as well as slightly below the transition and slightly above. Data are not obtained at high accelerations (white regions of plots).

appears but particles remain globally segregated. Fluctuational energy of hex-nuts in discotic regions, in which most hex-nuts are mainly standing on their ends, is slightly higher than in hexagonal regions, where most hex-nuts lie flat.

Throughout the accessible range in accelerations, $E$ grows monotonically with $\Gamma$, the only exception being at the highest acceleration where the motions of the smaller component, the spheres, decrease after reaching a maximum. This corresponds to a reduction in the motion of the more numerous beads, a phenomenon that is known to occur in dissipative granular systems [18]. While one might expect a large deviation in fluctuational energy indicative of phase separation, this is not observed. Even at the highest acceleration [Fig. 1(d)] where the local ordering of the hex-nuts is destroyed but global ordering remains, there is no major transition in the fluctuational energy profiles.

The second feature analyzed in this work is the effect of increasing solvent concentration on ordering. In microscale systems, ordering abruptly appears as the concentration of solvent increases. This is expected, for ordering is governed by the number of ways of rearranging the more numerous species [11]. Sharp transitions are also observed for our granular system. We establish the ordering state of the system by adopting an objective set of criteria, namely, a state is determined to be hexagonally packed if more than 50% of hex-nuts are associated with a hexagonal lattice, the state is taken to be discotic if multiple rouleaux containing four or more hex-nuts are present, and the state is determined to be segregated if more than 50% of the hex-nuts are segregated and disordered. In Fig. 3, we plot transitions between states as a function of sphere volume fraction and dimensionless acceleration for two different driving frequencies. Lines represent transitions that are clearly defined and differences in shading represent transitions that must be present but whose precise location is not defined by the present study.

All experiments are repeated three times starting from an initial state in which the granular blend is stirred by hand to reach, as nearly as attainable, a mixed condition. Steady-state patterns develop in between 1 and 5 min. All patterns described in the text are representative of steady-state conditions after 5 min of operation, though extended runs up to 30 min showed no discernable difference in behavior. Hysteresis is encountered, but starting from a highly energetic well-mixed state with no discernable patterns and decreasing the acceleration to the value of interest reproducibly produces an

unambiguous pattern. Over the course of several months the maximum acceleration necessary to produce the observed patterns monotonically increased by as much as 20%, though the qualitative behaviors shown are unchanged. The particle tracking experiments (Fig. 2) utilize aged beads, resulting in the appearance of hexagonal and discotic patterns at a larger acceleration range than those seen in Fig. 3. Comparable variations with particle wear and dirt accumulation have been previously reported in granular experiments [19].

The observed ordering depends on particle concentrations, although for the granular problem studied here, ordering dependence on mean energy and particle concentration is more rich than would be expected from colloidal or polymeric studies. At its simplest, we find that hexagonal states [Fig. 1(b)] form whenever the bed is agitated slightly above the static state. Additionally, discotic states [Fig. 1(c)] form at sphere concentrations of about $\varphi=38\%$. The onset of discotic ordering as $\varphi$ is increased may be a consequence of the formation of rouleaux increasing the number of structures that maximize free volume. On the other hand, the elimination of the discotic state as $\varphi$ is increased above about 40% is different, and the cause for this anomaly is unclear. Similarly at both 60 and 80 Hz, the hexagonally or discotically ordered states are destroyed as the acceleration is increased: at high $\Gamma$, our granular system displays a transition between mixed and segregated states as $\varphi$ is increased above about 25%.

Plotting the pair correlation function $g(r)$ of the solvent grains, a common metric used to describe the local structure of a granular material [12], quantifies the ordering of each of the patterns in Fig. 1. Plots for all four cases are shown in Fig. 4. The extent of geometric order of a blend is characterized by the magnitude of oscillations in $g(r)$. As shown in Fig. 4, the system with the greatest local order is the segregated state [Fig. 1(d)], followed by the comparable discotic [Fig. 1(c)] and hexagonal states [Fig. 1(b)], and finally the mixed state [Fig. 1(a)] exhibits the least order, i.e., has the shallowest peaks and valleys. It needs to be clarified that ordering of the solvent molecules does not imply ordering or pattern formation of the hex-nuts. This being said, this approach may enable characterization of transitions from completely disordered states to partially ordered states, shown by the noticeable difference between the $g(r)$ profiles for the segregated and hexagonal or discotic states. In order to fully characterize the system ordering, further work is needed to develop tools that reliably capture ordering of particles with
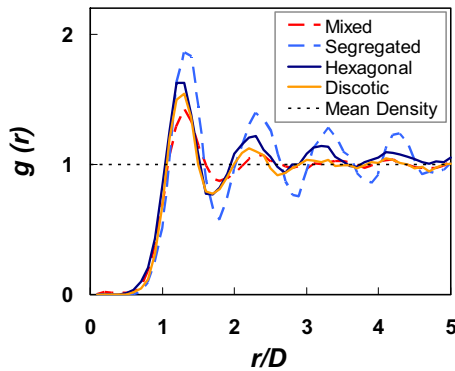
FIG. 4. (Color online) Pair correlation functions for observed patterns in the dotted rectangular regions in Fig. 1. Surface bead centers are marked by visual inspection and the pair correlation function is calculated with three point moving averages of 50 bins. Rectangular regions were hex-nut lean, which allowed us to isolate the length scales associated with bead-bead interactions. Choice of sample region location did not affect $g(r)$ profiles, excepting the hexagonal case, where there was only one bead-rich region.

regular shape (the hex-nuts) in addition to that of the uniform spheres.

In the segregated state, a large disordered region of hex-nuts is enclosed by a highly ordered packing of solvent grains. For the mixed state, there is minimal ordering of the spherical grains, shown by a $g(r)$ profile that quickly approaches the average system density. Presumably, the distributed hex-nuts disrupt the packing of the beads and destroy any long-range order. The ordering in the hexagonal and discotic states is similar, with the hexagonal state demonstrating slightly more order of the solvent grains. In addition, the hex-nut packing in the hexagonal state occupies most of the available domain, restricting the movement of the solvent beads, whereas the expanse of the hex-nut packing in the discotic state is much smaller, providing more room for the solvent grains. It seems plausible that the observed increase in solvent ordering may be the result of a depletion effect [11], with greater order occurring in the system with less room available for the solvent molecules to occupy.

However, the coexistence of two species of differing order at the same vibration conditions (ordered hex-nuts and disordered spheres) remains to be explained.

We note that increasing the concentration of spheres leads to a sharp increase in the acceleration necessary to form these structures. This is consistent with the behavior of small scale systems, as increasing the concentration of small particles in microscale systems leads to a decrease in the mobility of the larger particles and a higher temperature (energy input in our case) is required to free the larger particles from the small particle matrix in order to form structures [11]. The existence of a sharp transition with an increase in concentration has previously been observed in homogeneous granular systems approaching the fluid-to-crystal transition [12]. We expect that if the concentration could be increased further, without the creation of convection cells, the patterns would cease to form at any acceleration.

Unlike colloidal systems, the states described here appear in a nonequilibrium system under vibration and in the presence of gravity. Similar to colloidal systems, on the other hand, our experiments indicate that there are well-defined phase transitions between granular ordered states that appear to be governed by changes in particle concentration and fluctuational energy. This supports prior contentions that correlations between equilibrium thermodynamics and nonequilibrium granular physics may be found [8,17] and suggests that predictions for mixing, segregation, and other large-scale descriptions from basic considerations may be within reach. However, much work is still needed to overcome the challenges of applying traditional thermodynamic approached to nonequilibrium granular systems exhibiting non-equipartition of granular temperature. This work demonstrates that patterns that were previously limited to molecular colloids and microscale cells are also exhibited by macroscale granular materials.

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