Direct observation of stringlike collective motion in a two-dimensional driven granular fluid

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Dense ensembles of monodisperse hard spheres spontaneously assemble into regions of local crystalline order (grains) that are separated by relatively disordered grain-boundary (GB) regions. It is well known that grains and grain boundaries (GB) profoundly affect the material properties of polycrystalline materials and plastic deformation and transport in this ubiquitous class of materials can be particularly influenced by GB structure and dynamics. We experimentally investigate the nature of particle motion in the GB regions of a quasi-two-dimensional driven system of hard spheres and find, in accord with recent molecular-dynamics simulations of metallic polycrystalline materials, that particle motion in the GB regions involves a highly cooperative stringlike motion as in glass-forming liquids. Moreover, we show that the addition of small particles to a granular fluid allows the scale of this collective motion to be modulated, a phenomenon that is also observed in simulations and measurements on glass-forming fluids.

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I. INTRODUCTION

Many structural materials, including both polycrystalline and glass-forming materials, involve an admixture of well-packed local molecular or particle regions coexisting with more disordered regions having a relatively high local mobility. Effective modeling of the properties of these diverse materials requires an understanding of the implications of this packing heterogeneity and corresponding mobility heterogeneity on particle dynamics and material properties.

Recent efforts have focused on the characterization of dynamic heterogeneity in glass-forming fluids where stringlike collective motions (observed upon cooling in molecular fluids and upon increasing particle concentration in colloidal fluids) have been found to dominate molecular transport [1–7]. The growth of collective and relatively fast particle motion in strongly interacting fluids is accompanied by the growth of interpenetrating ramified clusters of relatively low mobility [9,10]. At low temperatures, both slow and fast structures become persistent and lead to a complex fluid rheology that is similar in many ways to that of associating fluids [12]. Two important aspects of collective particle motion are the spatial extent of this heterogeneity in molecular mobility and the fragility of the glass transition process. Fragility, in the context of the glass transition, quantifies how strongly the rate of structural relaxation changes with temperature and composition upon approaching the glass state. Fragility and dynamic heterogeneity are related phenomena, and can be affected by finite-size effects, additives and impurities, pressure, or other perturbations of the system that influence molecular packing [1,13]. In particular, simulations on glass-forming liquids [13] have indicated that small particles change the nature of glass formation (i.e., fragility) and thus change material properties substantially.

Recent simulations have indicated that the same type of cooperative dynamics may occur in polycrystalline materials where regions of crystalline order are interspersed by grain boundaries (GBs). The grains play the role of immobile particle regions in the glass-forming liquid. The simulations showed that the "disordered" or "amorphous" GB regions are characterized by stringlike collective motion with characteristics (e.g., size distributions of strings or average string length) that are essentially the same as for glass-forming liquids [14]. Simulations have also shown that this collective motion is directly reflected in the rate of GB motion in these polycrystalline materials [14].

The observation that GB dynamics are similar to supercooled fluid dynamics provides a powerful new perspective for the analysis of mechanical properties of polycrystalline materials. For example, it allows for an understanding of the large changes that are known to occur in polycrystalline materials under different types of mechanical strain (e.g., compressional versus extensional material deformation) [14].

Direct imaging of particle displacement dynamics [4–8] has been of great use in the study of glass-forming liquids, both to test predictions of computational molecular-dynamics simulations and to extend studies of particle dynamics into regimes not accessible by equilibrium molecular-dynamics computation. For example, studies of both spherical colloidal particle and granular fluid dynamics have confirmed the dynamic heterogeneity phenomena first observed in simulation. Collective motion has also been seen in a two-dimensional glass-forming granular fluid where large particles were excited into a fluidized state by air flow [15].

The present work focuses on two computationally predicted phenomena. First, we explore the existence and nature of the predicted collective motion in the GB regions [14], and second we consider the extent to which this collective motion might be modulated by the addition of small spheres. We utilize a simple two-dimensional granular fluid system consisting of hard spheres that are densely packed in a single layer. When the spheres are of the same size, regions of hexagonal order, which we will denote as grains, form spon-

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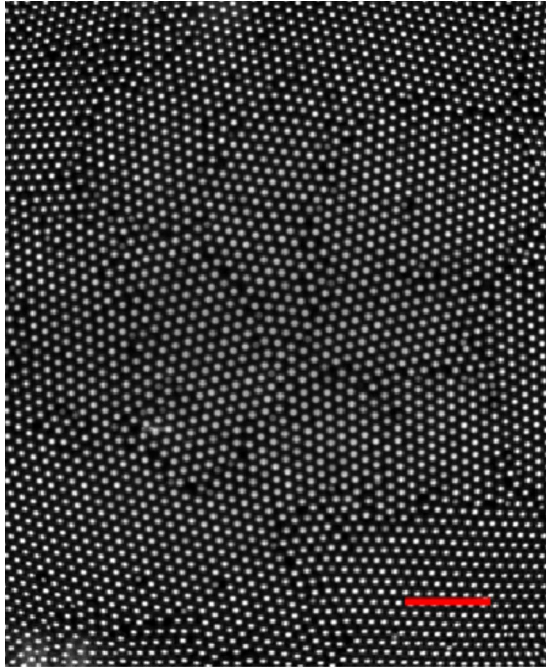†Corresponding author: wlosert@umd.edu

FIG. 1. (Color online) Polycrystalline film for low concentrations (3%) of small particle additives. The regions of hexagonal order (grains) are large, separated by narrow disordered GBs. Particles are touching, but appear as points due to the imaging method used. Small particles are less bright than large particles in the image. The red (gray) line in the lower right corner is 2 cm in length.

taneously, and the system rapidly converts to an ordered state, i.e., crystallizes. The particles are excited into motion via shaking ("thermalized") under conditions where the "fluid" remains nearly two dimensional [9–11]. In our measurements, we ensure that our samples remain polycrystalline by using a small amount of smaller spheres to modulate the grain structure and thereby frustrate long-range ordering. A similar system had been systematically investigated before theoretically by Onuki and co-workers [16].

We first describe the experimental system used to test these predictions and then describe our analysis of the experiments, focusing on the geometry of the grains and GB regions and the collective stringlike motion in the GB regions.

II. EXPERIMENTAL

The experimental system consists of a system of hard spheres (3-mm- and 2-mm-diameter chrome) confined to a horizontal quasi-two-dimensional circular container (146 mm radius) shaken vertically. An illustrative particle configuration is shown in Fig. 1. The vertical shaker was operated at 125 Hz at amplitudes to generate 4.5g peak acceleration, where g is the acceleration due to gravity. The container lid was 0.1 mm higher than the large particles to allow for horizontal motion of all particles while preventing stacking of multiple layers. The walls of the shaker were made of aluminum to minimize energy loss during collisions with boundaries. The lid was made of acrylic and the base of

Delrin. A high-speed camera, placed above the shaker, took pictures at 125 frames per second (fps) in close synchrony with the vibration frequency of the shaker, though the relative phase of shaking and imaging was not controlled.

Before each experiment, the lid of the container was removed and the system was strongly shaken to uniformly distribute small particles throughout the surface. Two sphere sizes used were made of the same metal to eliminate the possibility of segregation due to the different material properties. Image acquisition (over 32.7 s) was started within less than one minute after the shaker was started.

We performed two general types of experiments on our model driven granular fluid. Both types consisted of five extended measurements, each for a range of values of the area ratio of the small to large particles. In the first set, the total area coverage was held constant. To calculate the area coverage the spheres were projected into the plane as a circle of the same radius. The area coverage studied was 0.85 of the total area (area fraction), close to the 0.91 coverage obtainable for hexagonal close packing, i.e., a single grain covering the whole container. In the second set of experiments, the area coverage was again 0.85 initially for a monodisperse large particle system, and the area coverage was then increased by adding small particles. The purpose of the present work is to characterize the nature of the particle motion in the GB regions of these driven granular fluids and to show how this collective dynamics can be modified by the addition of small particles.

III. RESULTS

A. Crystallization and GBs

Two dimensional driven systems of equal-sized hard spheres are known to order into a hexagonally close-packed state [17]. As evident from Fig. 1, at an area coverage of 0.85, about 6% less than optimal hexagonal close packing, locally ordered regions ("grains") of high density are visible, but interspersed by relatively poorly packed, lower density regions that constitute the GB.

When small particles are added (at constant area coverage), the grains decrease in size, and the small particles concentrate in the grain boundaries. Figure 2 clearly shows that as more small particles are added, grains decrease in size. In the remainder of the paper, we analyze the static structure and dynamics of the particles within the grains and GB.

B. Quantification of grain and GB properties

The GB regions can be visualized using a simple measure of local order in two dimensions and the property that these regions are significantly more disordered locally than the grains. To determine the location of the GB regions in our system, we used the following algorithm. First, we identified the six nearest neighbors of each particle that are at least two particle diameters from the boundary of where data were acquired so as to assure that the particle's six closest neighbors are equally distributed around it. We then calculated the angle of the link to all six neighbors relative to an arbitrary
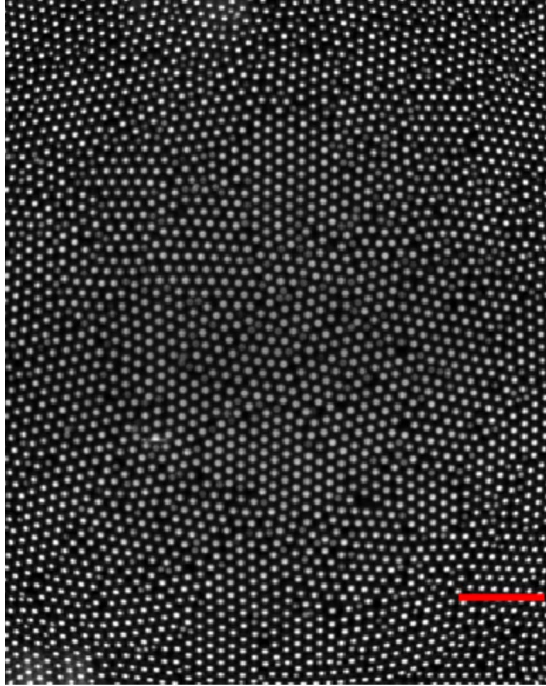
FIG. 2. (Color online) Polycrystalline film for a higher concentration (10%) of small particles than Fig. 1. The size of regions of hexagonal order (grains) decreases with an increase in the small particle concentration. The GB regions increase in area. The red (gray) line in the lower right corner is 2 cm in length.

reference axis. These angles were then summed according to the relation [17]

$$\psi_6 = \left| (1/n) \sum_{i=1}^{n} e^{i6\theta_i} \right|, \quad (1)$$

where θ is the angle and the summation runs over the six nearest neighbors [17]. Deviations of ψ_6 from 1 can be taken as a measure of disorder that can be used to locate the GB regions. In particular, we take the somewhat arbitrary condition $\psi_6 < 0.7$ to define the GB. The large difference in the degree of order between the grains and the GB make our results rather insensitive to the precise value of this cutoff value.

Figure 3 shows the results of applying this algorithm to our particle data. The purple circles correspond to regions of hexagonal close packing (i.e., grains). We see that at low small particle concentrations that the system arranges itself into large grains with well-defined but relatively poorly ordered GBs. This trend was noted before in the simulations of Onuki and co-workers for binary hard disk mixtures in two dimensions [16].

Over the time scales of our experiments, the particle flux out of the selected measurement area was nearly zero and the net displacement of GBs was similar for low and high small particle concentrations. It is noted that the time scale of the experiment is not long enough to properly characterize GB motion so any conclusion as to the magnitude of GB displacement over longer time scales is not possible in our mea-
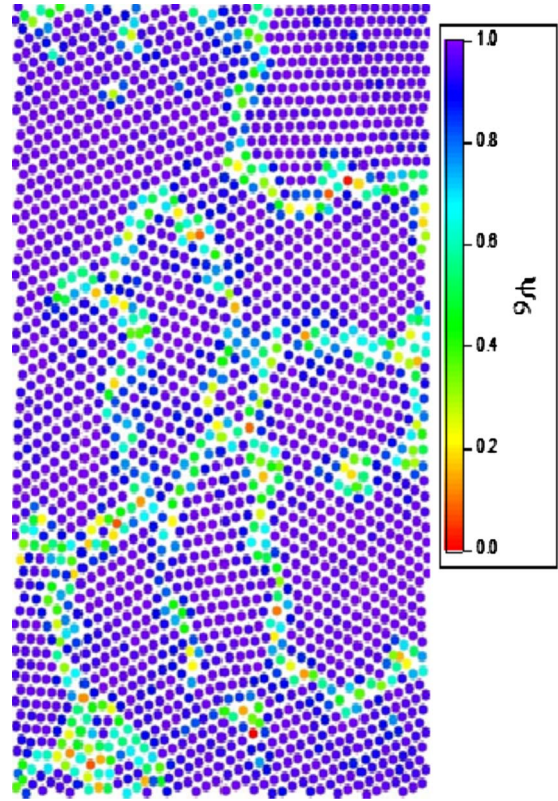

FIG. 3. (Color online) GB regions determined using the algorithm of [16]. Purple (dark gray) signifies near hexagonal particle packing. Red (light gray) corresponds to a more disordered packing (i.e., GB regions). Small particle concentration is 3%.

surements because of the long-time scales required for the estimation of the GB mobility.

In order to quantify the variations in local order in Fig. 3, we determined the area occupied by the GB regions. Using the already identified GB particles, the Voronoi area of each particle was calculated [18] and these areas were summed to determine the total GB area. As expected, the GB area increases as the total order of the system decreases, or as the concentration of the small particles increases (Fig. 4). Both the total GB area and GB location did not change significantly on the time scales of our measurements.

C. Stringlike cooperative motion

Using a method similar to that described in [1,3,13,14], the existence of collective particle motion was determined. We first identified the "mobile particles" as those particles that undergo a greater displacement than would be expected in a Brownian fluid having the same long-time diffusion coefficient. The precise definition of these particles has been described repeatedly before [1,3,14], and in simplified terms these particles are essentially the 5% fraction of particles that have undergone greatest particle displacement after a diffusive decorrelation time t* (peak of non-Gaussian parameter) at which the deviation from Brownian particle displacement is greatest. Mobile particles exhibiting cooperative motion remain in proximity on a scale on the order of the interpar-
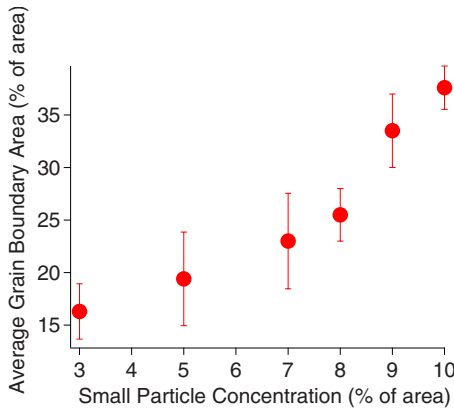
FIG. 4. (Color online) Average grain-boundary area as a function of additive concentration of small particles, defined as the percentage of total area covered by the small particle additive. Each data point is the average different initial configurations. Total area is 285 cm^2

ticle spacing throughout the course of the particle displacement, and the collective motions in our measurements are found to take the form of polymericlike structures or "strings," as in previous simulations of glass-forming liquids and polycrystalline materials [1,3,13,14]. The determination of the average string length for various small particle concentrations was again determined exactly as in previous studies [1,13] so our discussion of the method is brief. We stress that there is no discrimination between large and small particles in the string length analysis.

D. Strings are localized to GB regions

Overlaying the mathematically determined strings with the GB regions reveals that strings primarily organize inside the GB regions. Previous molecular-dynamics simulations of the dynamics of GB in Ni also revealed the existence of strings in GB regions so the effect is apparently general [14]. Figure 5 shows a visualization of the GB regions with the same color map as in Fig. 3, the black spheres here denoting particles that are in strings. We find that at least 95% of all strings are in the GB.

In addition, stringlike motion was observed to occur more frequently in GB with low local order, and in regions of high small particle concentration. The variability of the local GB order, the extent to which the strings are localized in GB regions with low local order, and the localization in regions of high small particle concentration (regions denoted by black circles) can be observed in Fig. 5. However, the statistics are not sufficient to quantify these observations.

E. Quantification of GB stringlike motion

Since nearly all strings are found to be located in the inside of the GB regions, the average number of strings per frame, as well as their lengths inside the GB, is nearly the same for strings within the GB as for the system. We then focused our analysis on the strings within the GB. First, we note that as more small particles are added, the average number of strings in the GB increases as shown in Fig. 6. Simi-
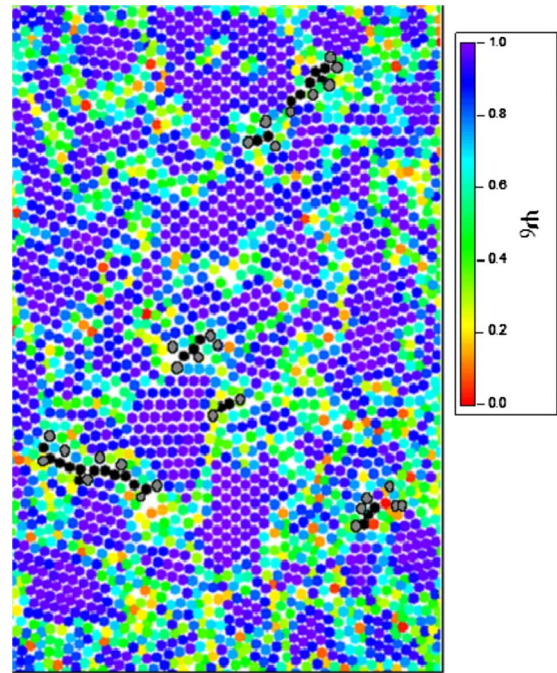

FIG. 5. (Color online) String localization in grain-boundary region. Black circles are particles that belong to strings, while gray circles outlined in black are small particles located near strings. We find that the number of strings increases with the concentration of the small particles. The other colors are the same as in Fig. 3. Small particle concentration is 10%.

larly, the average length of each string increases as more small particles are added, as illustrated in Fig. 7. Since GB area is proportional to small particle concentration, our results can also be described in terms of the increase in the GB area. Each data point is the average of ten time steps from a single experiment. Since the strings are relatively short-lived on the time scale of our experiments, no string is included in more than one time step. Both plots are approximately linear and extrapolate to zero in the limit of a vanishing small particle concentration.
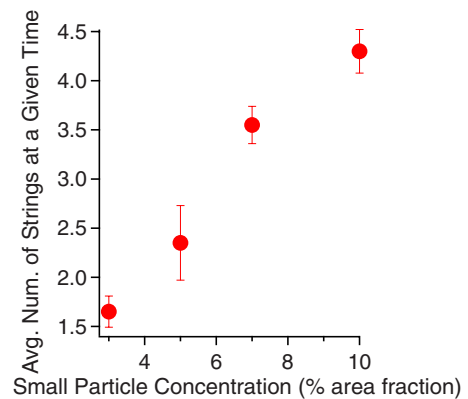

FIG. 6. (Color online) Average number of strings at a given time step as a function of additive concentration, defined as the percentage of total area covered by the small particle additive. The uncertainties are the standard error from measurements taken during one experiment at one randomly selected time and at 1.6 s intervals after that time.
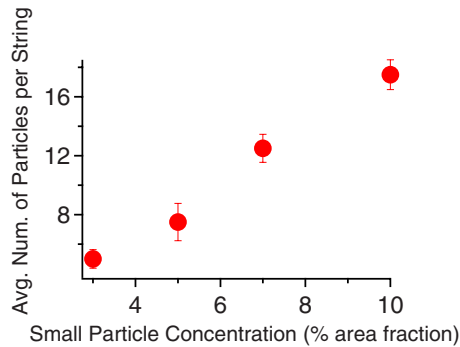
FIG. 7. (Color online) Average string length as function of additive area coverage, defined as the percentage of total area covered by the small particle additive. The uncertainties are the standard error from taken during one experiment at one randomly selected time and at 1.6 s intervals after that time.

IV. CONCLUSIONS

We have directly observed the existence of computationally predicted [14] stringlike collective particle motion in a model polycrystalline material, and we have shown that the collective motion is localized to the GB regions of the material.

The driven granular spontaneously forms a system of grains separated by GB regions that evolve slowly with time so there is no significant change in grain-boundary area over the 30 s course of each experiment. Measurements of the properties of the GB, such as their area, require the averaging over many granular fluid experiments. The strings, on the other hand, are more dynamic structures, having a lifetime on the order of 0.1 s in our measurements. The relatively fast evolution of the strings allows for the determination of the metrical properties of these structures since a single experiment provides a large ensemble of such structures for property averaging.

We find that the addition of small particles significantly affects the behavior of the polycrystalline material. These particles obviously increase the width and overall area coverage of the grain boundaries where the small particles tend to be localized. Small particles are naturally excluded from the grain regions since these particles do not fit into lattice substructure of the grains. We also observe that the scale of collective motion can be modulated with small particle additives, as in glass-forming liquids [14]. Unexpectedly, we found that the addition of small particles *increased* the scale of collective motion (average number of particles in a string); the opposite effect was found in model polymeric glass-forming liquids with small molecule additives [13].

Collective, stringlike motion is not only interesting as a structural phenomenon of strongly interacting fluids, but these collective motions are expected to have a large influence on rate processes and mechanical properties of polycrystalline materials. For example, our observations of collective motion in our model granular "fluid" should provide new insights into how polycrystalline materials deform, and how their properties may be affected by changes in materials composition. The observation of more and longer strings upon addition of small particles points to the possibility that other additives may enhance or decrease the number and length of strings (depending on particle shape and size) in other polycrystalline materials by altering the global particle packing and thus affect materials properties substantially.

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