Gases, liquids and crystals in granular segregation

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Abstract. – We report the results of an experimental investigation of segregation in a binary mixture of dry particles subjected to horizontal oscillatory excitation. The thin layer of particles was driven by the stick–slip frictional interaction with the surface of a horizontal tray. As the packing fraction of the mixture was increased the evolution of distinct phases was observed. We identified them as a binary gas, segregation liquid and segregation crystal and provide both microscopic and macroscopic measures to identify their properties. Finally, we draw some analogies between segregation in our granular system and self-assembly in binary colloidal mixtures.

In segregation, excitation via flow or shaking can, counter-intuitively, cause an initially homogeneous mixture of grains to de-mix [1, 2]. Despite decades of research into the phenomena [3], a predictive model of the processes involved has yet to emerge. More recently, segregation has received considerable attention from the physics community as an example of a challenging far from equilibrium system [2]. Although a variety of geometries has been explored [4–6] and many mechanisms proposed [7, 8], an understanding of the fundamental principles involved remains incomplete. This is surprising considering that a better understanding would have a major economic impact in the pharmaceutical, chemical processing and civil engineering industries. For the class of quasi-2D binary granular systems a qualitative segregation mechanism has been suggested [9–11] using the idea of *excluded volume depletion* as in colloidal systems and binary alloys [12]. This is in the spirit of the physics of complex systems where attempts have been made to unify descriptions of granular materials, colloids, gels and foams [13, 14]. We discuss the relevance of these ideas to our observations in some concluding remarks.

Here we report the results of an experimental study of granular segregation in a thin layer of a mixture of two particle types which lie on the surface of a horizontally oscillated tray. The tray was $180mm$ in the direction of the oscillation and $90mm$ wide and the shallow binary

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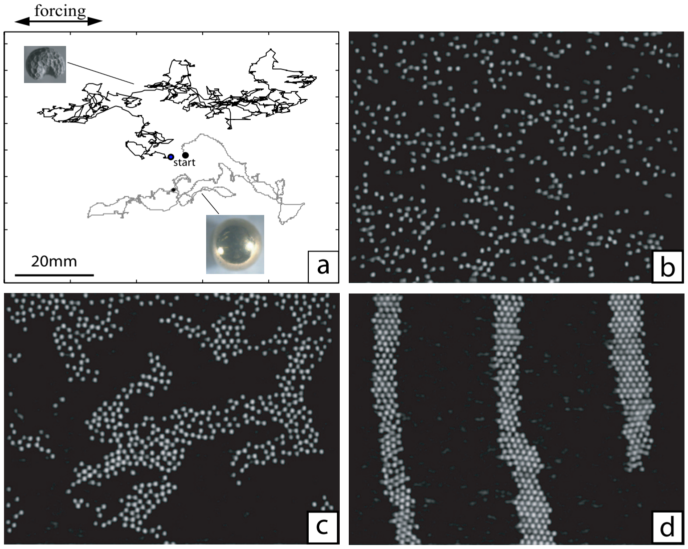

Fig. 1 – (a) Stochastic trajectories taken over a period of 1 min for a single particle on the tray. The black and grey trajectories (poppy seed and phosphor-bronze sphere, respectively) show two quasi-random walks on the oscillating surface. The distributions of step lengths are exponential (poppy seeds) and gaussian (spheres) [15]. The three photographs correspond to states within the various phases: (b) binary gas ($C = 0.516$), (c) segregation liquid ($C = 0.729$) and (d) segregation crystal ($C = 1.071$). The binary layer was started from mixed initial conditions in each case and frames were taken after 3min of shaking so that a (macroscopic) quasi-steady state was achieved. Note that only the phosphor-bronze spheres are visible.

granular mixture was approximately one particle deep. The particles used were monodisperse phosphor-bronze particles which were smooth high-precision spheres of diameter $1.5mm$ and density $8.8gcm^{-3}$ and poppy seeds which were rough non-spherical particles with average diameter $1.07mm$ and density $0.2gcm^{-3}$. The poppy seeds had a measured polydispersity level of 17%. The size ratio for the two types of particles used was $q \sim 1.07/1.5 = 0.71$. The vibration was sinusoidal to within 0.1%, unidirectional with fixed frequency $12Hz$ and amplitude $1.75 \pm 0.01mm$ and was monitored using accelerometers. A reasonable approximation to a two-dimensional system was achieved, as only a small degree of overlap of the poppy seeds occurred. This arrangement enabled us to image the entire system using a CCD digital camera and perform particle tracking of the phosphor-bronze spheres. High image resolution was required for the microscopic measures and, for these, we focused on a central $(76 \times 62)mm$ area of the layer.

Two further features of our set up were that the horizontal geometry minimized compaction effects due to gravity and the particles were always in contact with the excitation provided by the oscillatory tray. While the forcing was strictly sinusoidal, both types of particles were driven by a stick-and-slip interaction with the driving surface, resulting in anisotropic random motion in two dimensions. Evidence for this can be seen in the single particle trajectories shown in Fig. 1a. In addition, the statistics of the motion were anisotropic with a preference for motion in the direction of the forcing. Note that the two types of particles respond to the driving differently, which presumably arises from a combination of the differences in mass, shape and surface properties. Details of the statistical analysis of the particle trajectories will be presented elsewhere [15]. Clearly, the collective behaviour when many particles are present will be modified. A simple test was carried out by observing the motion of a coloured line within a monolayer of non-spherical particles. This provided evidence for diffusion, faster in the direction of the applied forcing.

The parameter space of the system is large and we have chosen to explore the effect of the total filling fraction of the mixture, which was previously shown to be a key control parameter [17]. We denote this by *layer compacity* defined as, $C = (N_1 A_1 + N_2 A_2)/(xy)$, where N_1 and N_2 are the numbers of poppy seeds and phosphor-bronze spheres in the layer, $A_1 = (0.90 \pm 0.15) mm^2$ and $A_2 = (1.77 \pm 0.06) mm^2$ are the two dimensional projected areas of the respective individual particles and x and y are the longitudinal and transverse dimensions of the tray. The uncertainty associated with the measurements of C is approximately 8%. Note that our criterion for a quasi-two dimensional system is that the phosphor-bronze spheres remain in the monolayer regime but, at the highest compacities, the poppy seeds can overlap up to a maximum layer height of $1.5mm$, i.e. the diameter of the larger spheres. Hence, our compacities can be higher than the maximum packing value in two dimensions. The compacity was varied by incrementally increasing N_1, while keeping $N_2 = 1596$ constant. Experiments showed that the phase behaviour is robust over a range of phosphor-bronze spheres.

Analysis of the segregation domains, in previous work [17], suggested the existence of a single continuous phase transition of granular segregation such that there is a critical compacity point, C_c, below which segregation does not occur. Here we present new evidence that a connection with equilibrium phase transitions may be deeper by uncovering three qualitatively distinct segregation phases which can be related to behavior observed in binary colloidal systems.

In Fig. 1(b,c,d) we present snapshots of three states of the granular layer, at different values of C, representative of the three distinct phases of granular segregation. These were obtained in experimental runs which were consistently started from homogeneously mixed initial conditions and only the compacity was varied between each realization. At low C, Fig 1b, a '*binary gas*' was found, i.e. this was a collisional regime where segregation did not occur. At intermediate C, Fig. 1c, clustering of the larger particles occurred and mobile segregation domains formed. The movement of the clusters across the granular layer was reminiscent of oil drops on water as they flowed, merged and split; the motion of the particles within the clusters was highly agitated. We denote this by '*segregation liquid*'. At high C well defined immobile stripes formed perpendicular to the direction of forcing. Within these segregation clusters, the spheres crystallized into an ordered hexagonal lattice, Fig 1d. We denote this phase by '*segregation crystal*'. We stress again that these segregated states resulted from a self organization of the granular layer, having started from a homogeneous mixture.

In order to classify these phases we measured three quantities: one 'macroscopic' (i.e. at the domain level) and two 'microscopic' (i.e. at the particle level and determined by the positions of the large spheres). Macroscopically, we studied the fluctuations of the average width for the domains of phosphor-bronze spheres. At the microscopic level we measured both the particle radial distribution function and the local density for the spheres.

In Fig. 2a we present 10min long time-series of the average width of the domains, ϕ as measured in [17], for three values of the compacity which are representative of each of the segregation phases. In the binary gas phase, at low compacities, ϕ shows no evolution since the binary layer remains in a mixed state. At high compacities, ϕ exhibits a fast initial segregation growth which is followed by saturation as stable crystalline segregation domains form. At intermediate compacities, in the segregation liquid phase, after the fast initial growth, ϕ slowly coarsens due to splitting and further merging of the domains. This is consistent with *liquid*-like behaviour. However, a separation of two distinct time scales is clearly present and

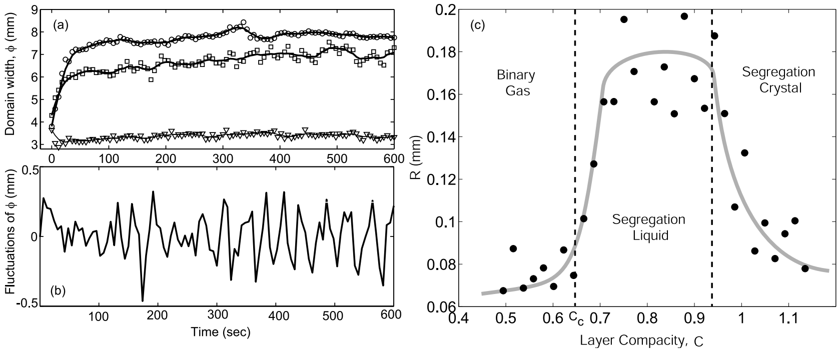

Fig. 2 – (a) Time-series of, $\phi(t)$: (▼) for $C = 1.028$ (■) for $C = 0.751$ and (•) for $C = 0.580$. We filtered $\phi(t)$ through a digital low-pass finite impulse response (FIR) digital filter algorithm with brickwall at $\omega = 2.29 \times 10^{-3} Hz$ and $-3dB$ point at $\omega = 9.78 \times 10^{-3} Hz$ to obtain $\phi_{filtered}(t)$ (solid curves). (b) Time series of the macroscopic fluctuations, $f(t) = \phi(t) - \phi_{filtered}(t)$ for $C = 0.751$. (c) Root-mean-square of the fluctuations, R, plotted as a function of C. The dashed line at $C_c = 0.647$ denotes the binary gas - segregation liquid transition point C_c measured in Ref. [17]. The dashed line at $C = 0.943$ is a guide to the eye for the possible location of the segregation liquid to crystal transition. The solid grey line is a guide to the eye.

we focus on the resulting regime reached after the fast initial segregation. The data for the microscopic measures presented below was acquired for a period of 1min and obtained 3min after the driving was switched on.

Firstly, we monitor the behaviour of the segregated domains using a macroscopic measure. We focus on the macroscopic fluctuations of, $\phi(t)$. This was high pass filtered to remove the slow dynamics of the domains and thereby obtain their fluctuations, $f(t)$, directly. An example of $f(t)$ for $C = 0.751$ is presented in Fig. 2b. The fluctuations provide a measure of the collective noise which arises from the merging and breaking dynamics of the domains. The RMS of these fluctuations, $R = \sqrt{\langle f(t)^2 \rangle}$, is plotted as a function of C in Fig. 2c. At low values of C no segregation clusters form and R is low but as the critical point, C_c, is approached, the fluctuations of the domains grow rapidly as mobile clusters form in the segregation liquid regime. As C is increased further, R abruptly decreases when stable crystalline stripes form (see Fig 1d), suggesting a segregation liquid to crystal transition.

It is now of interest to relate this macroscopic behaviour to the structural configurations of the spheres as measured by the radial distribution function,

$$g(r) = A(r) \langle \sum_i \sum_{j \neq i} \delta(r - r_{ij}) \rangle, \tag{1}$$

where r_{ij} is the separation between the i and jth particles and the angled brackets denote a time average for the 1min of data acquisition. $A(r)$ is a normalization constant such that $g(r) = 1$ for a uniform distribution of particle positions. In Fig. 3(a,b,c) we show three curves of $g(r)$ corresponding to the the snapshots (b,c,d) presented in Fig 1, respectively. For the binary gas (Fig. 3a), $g(r)$ has a peak at $r/d = 1$ which quickly decays at large distances, as expected for a disordered gas. Increasing C results in a monotonic increase of the height of the first peak, $g(d)$, consistent with an increasing effective attractive potential. At intermediate C (Fig. 3b), *liquid-like* behavior is observed, with $g(r)$ peaked at 1, 2 and 3 particle diameters. The positions of neighbouring spheres are correlated and the maxima may be associated with

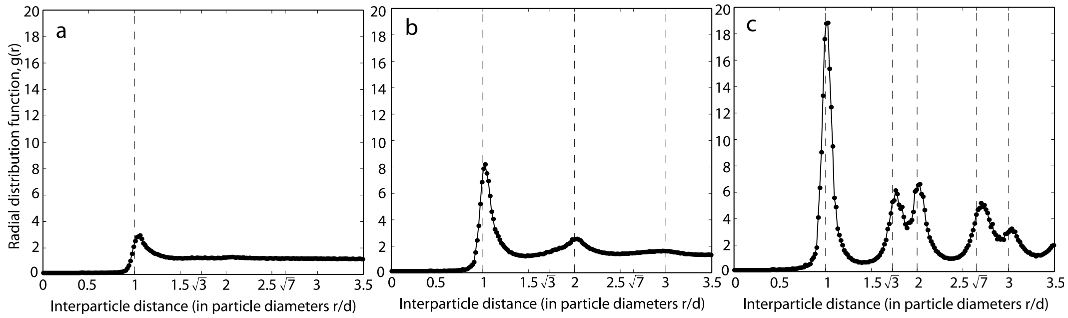

Fig. 3 – Radial distribution functions, $g(r)$, for states in each of the segregation phases: a) binary gas (C=0.516), b) segregation liquid (C=0.729) and c) segregation crystal (C=1.071). The vertical dashed lines correspond to the expected location of the peaks in each of the segregation phases. Note that the image processing and finite pixel size of the camera 'blur' the distributions slightly, which accounts for the non-zero value of $g(r)$, for $r < d$.

concentric shells of neighbours. The oscillations are rapidly damped, showing the decay of short-range order. This behaviour is commonly seen in hard sphere liquids and was first observed experimentally by Bernal [18]. In the segregation crystal phase, at high C, (Fig. 3c) two further peaks are observed near $r/d = \sqrt{3}$ and $r/d = \sqrt{7}$, characteristic of a static hexagonally packed crystal, in two dimensions. All peaks are slightly offset due to the rattling motion of the spheres.

Having presented structural information, we now turn to a discussion of the local density of the large spheres which was calculated using Voronoi tessellation [19]. The local density was defined as the ratio between the sphere's projected area, $\pi(d/2)^2$, and the area of its Voronoi polygonal cell. This provides a particularly clear measure of the transition between the binary gas and the segregation liquid phases. We obtained Probability Distribution Functions (PDF) of the local density by analyzing 1500 temporal realizations (at $25Hz$), within the central region where each realization contained $\sim$ 500 spheres. A typical example of such a PDF is shown in Fig. 4b. At a particular C, we extracted a characteristic local density, ρ_v^{max}, from the density value at which the peak of the PDF occurred (Fig. 4c). The width of the PDF, w (Fig. 4c) is a measure of the local density fluctuations associated with individual spheres contrasting with the macroscopic fluctuations which arise from the collective motion of the domains. When the transition from binary gas to segregation liquid occurred, by increasing C, ρ_v^{max} grew rapidly as segregation domains formed and there was a significant amplification of the microscopic density fluctuations at the particular value of $C_c = 0.665 \pm 0.049$. Close to the segregation transition, neighboring configurational states coexist and single large spheres were observed to migrate between segregation domains. This rapid growth of an order parameter combined with amplification of fluctuations is characteristic of equilibrium phase transitions [20] giving evidence for the existence of a critical point for segregation [17]. A further indication of critical behavior is provided by a time-series of the local density for a typical individual sphere. Close to this transition point, a large section of the range of possible local densities ($0 < \rho_v \leq \pi/\sqrt{12}$ for disks in 2D) is explored as seen in trace II in Fig. 4a). On the other hand, a typical time-series in the segregation crystal regime (trace III in Fig. 4a) illustrates that the particles within the crystalized segregation domains rattled inside cages formed by their hexagonally packed neighbors, yielding small fluctuations about a characteristic high local density which is indicative of a thermalized crystal.

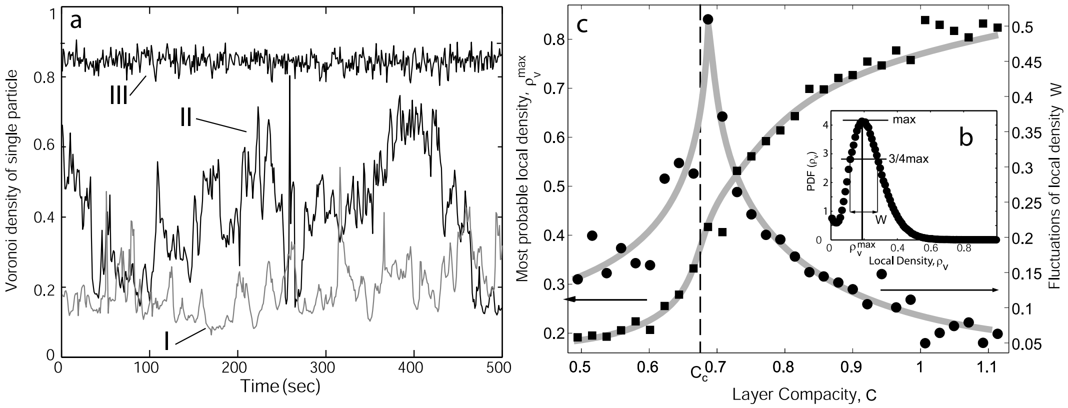

Fig. 4 – Local density. (a) Time series of the local densities for a typical individual sphere, illustrating the characteristic fluctuations, for the binary gas ($C = 0.578$, trace I), segregation liquid ($C = 0.687$, just above C_c, trace II), and segregation crystal ($C = 1.071$, trace III) phases. Inset (b): For each value of C data, 750000 particle positions were used to construct a PDF for the local density. (c) From this $PDF(\rho_v)$ we extract the characteristic, i.e. most probable, local density, ρ_v^{max} (squares) and the width gives an estimate of the microscopic fluctuations, w (circles). The dashed line is drawn at the critical compacity value, C_c , measured in Ref. [17] and the solid grey lines are guides to the eye.

The binary gas to segregation liquid transition occurs at a critical compacity of $C_c = 0.665 \pm 0.049$. It is interesting to point out that this value is close to the order-disorder transition in a two dimensional hard sphere system, which occurs at a filling fraction of 0.65 for equally sized particles [21].

We note that there are analogies between segregation in our binary granular system and aggregation in binary colloids [22] and emulsions [23] where the ordering is not restricted to differences in size but can also result from variations in shape or flexibility [24]. In particular, when the size ratio between the large colloidal particles and the radius of gyration of the polymer is $q \gtrsim 0.3$, colloid-polymer mixtures display colloidal gas, liquid and crystal phases of the large spheres [16, 25]. This is consistent with the value of $q = 0.71$ in our granular system.

Aggregation in colloidal systems is usually explained using an excluded volume depletion argument introduced by Asakura and Oosawa [26, 27] in the context of binary hard spheres. This entropic argument is equivalent to the mechanistic view that if two large particles are close enough so that no other particle (or polymer) may fit between them, they will be subjected to an asymmetric osmotic pressure that leads to an effective attractive inter-particle force. Our experimental procedure of increasing the number of poppy seeds while keeping the number of spheres constant is analogous to changing the concentration of the polymer in solution in colloid-polymer mixtures. This deepens the inter-particle potential U and decreases the overall temperature T but has the combined effect of increasing the dimensionless parameter U/k_BT [16]. The strength of the interaction can thereby be tuned to induce gas-to-liquid and liquid-to-crystal transitions [28]. While we also observe qualitatively similar changes in behaviour, our system is driven, dissipative and far from equilibrium. In addition, Brownian motion is an intrinsic part of the equilibrium dynamics of colloidal systems. Hence a direct connection between the two systems remains speculative.

In conclusion, our results provide quantitative evidence for the existence of three phases -

binary gas, segregation liquid and segregation crystal - in granular segregation of horizontally excited binary mixtures. We have presented both macroscopic and microscopic measures which are self-consistent. Direct analogies of this phase behaviour may be drawn with other depletion driven self-assembling binary systems, in particular colloid-polymer mixtures. This raises the possibility of importing ideas from binary colloids in equilibrium to formulate new models for granular segregation.

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