STATISTICAL MECHANICS AND REVERSIBLE STATES IN QUASI-STATIC POWDERS

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ABSTRACT

In a static granular material all particles are touching their neighbours and given a sufficiently high packing fraction a jammed state results. The configurational space of such states can be explored by tapping the packing and ramping the tapping amplitude and frequency. A statistical-mechanical approach which employs compactivity concept is offered for the description of relaxation of such states along the reversible branch of the packing fraction vs tapping amplitude diagram. We present recent experimental findings which confirm the existence of the reversible regime in the response of a granular material to tapping.

1 INTRODUCTION

Granular materials, such as powders, possess properties which render them different from systems described by classical statistical thermodynamics. The dissipative nature of the interparticle interaction means that inelastic collisions and frictional rolling require the energy to be supplied by external driving sources such as shearing or tapping. The typical physical dimensions of grains make the thermal energy per particle negligible compared with the gravitational energy so that after its deposition a granular packing is usually trapped in some "metastable" state which if perturbed exhibits irreversible and non-equilibrium rheological behaviour. Therefore in order to understand such complex behaviour of granular media one needs first of all to study situations which are perfectly characterised, and the character of the problem must be at a level of simplicity that physical laws can be indeed expected. This simplicity in turn implies circumstances which, though easy to idealize in a *gedanken experiment*, are not easy to create in a laboratory, indeed are such that great care needs to be taken to deal with cases which may seem rather artificial. We argue that it is in principle possible to develop a statistical-mechanical approach which describes such idealized granular media. Although the number of particles in a molar solid given by the order of magnitude of Avogadro constant $N_A \sim 10^{23}$ is a much larger number than $N \sim 10^8$ (which is the number of grains in a typical experimental powder sample), nevertheless N is usually very large. This implies that statistical-mechanical concepts of ensemble averaging should work at least in packings of hard grains where the entropy and volume, constrained by inability of particles to deform and overlap, are the governing quantities which form an intensive parameter analogous to temperature [1]. The necessity of having such "effective temperature" and the averaging formalism based on this intensive quantity for idealized models of powders, and establishing its applicability limits to the "real" granular materials, is indeed obvious. Recent vibration-induced compaction experiments [2]-[4] have provided a crucial insight into the applicability of the statistical-mechanical approach to granular materials by identifying the reversible regime in the density (i.e. the packing fraction) response to tapping. This reversible behaviour appears to be a sufficiently generic phenomenon since it has been observed for cohesionless monodisperse spheres [2]-[5] and rods [4]. We present experimental measurements of the electrical conductivity of vibrated slightly polydisperse packings made of irregularly shaped graphite and iron particles and demonstrate the existence of the reversible branch in the conductivity vs tapping amplitude diagram.

2 THE PROBLEM

2.1 Compactivity and the Zeroth Law Analogy

In conventional thermodynamics the zeroth law states the existence of temperature i.e. if when A and B touch and no heat flows between them, and if when A and C touch likewise, then no heat flows from B to C i.e. there exists a property, the temperature T, such that if $T_A = T_B$ and $T_A = T_C$ then $T_B = T_C$. Consider this *gedanken* experiment (see Figure 1). In a tube, powders A and B are confined by barriers at the ends and separating them. A regime of tapping is applied to A, B (say 10^3 taps of force g) and the barriers at the ends of A and B are allowed to move so that the powders A and B just fill the tube as shown. Now repeat with the same tapping regime, but this time with powder C in place of B. Now replace A by B and again perform the same tapping regime. Then one expects the lengths of powders to match as shown in the figure. This experiment may look like a dull one and most readers would say that it is obviously in accord with experience, but it must mean that there is some variable, call it X, which obeys an analogue of the zeroth law of conventional thermostatics:

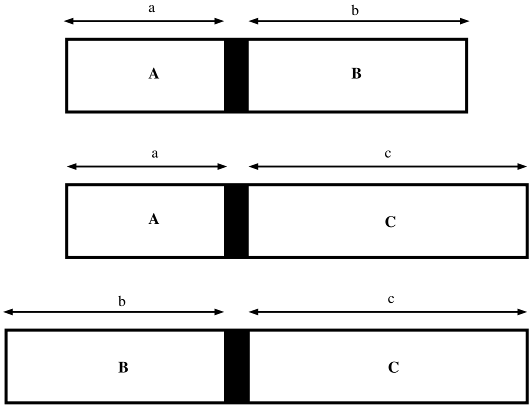

Figure 1: "Zeroth Law" Experiment: $X_A = X_B$ and $X_A = X_C$, hence $X_C = X_B$.

$$X_A = X_B, \quad X_A = X_C \Rightarrow X_C = X_B\,, \tag{1}$$

We call this variable the compactivity , and will argue that just as for thermal statistical mechanics

$$T = \frac{\partial E}{\partial S}\,, \tag{2}$$

where E is the energy, for powders we need

$$X = \frac{\partial V}{\partial S}, \tag{3}$$

where, as ever, the entropy S is the logarithm of the number of ways one can configure N grains into the volume V.

2.2 The Concept of Entropy

In statistical mechanics as against pure thermodynamics, the second law proclaims the central position of entropy, and defines it by

$$S = k \log \int \delta\Big(E - H(p,q)\Big)\, \mathcal{D}p\, \mathcal{D}q\,, \tag{4}$$

where E is the energy and $H(p,q)$ the Hamiltonian. Entropy S is function of internal energy E, the number of particles N and volume V. The analogue of (4), i.e. the "microcanonical" ensemble for jammed configurations gives

$$S = \log \int \delta\Big(V - W(\zeta)\Big)\, \Theta(\zeta)\, \mathcal{D}\zeta\,. \tag{5}$$

where entropy is now function of number of particles N and volume V. For the granular system with zero kinetic energy we *postulate* a phase space defined by collective coordinates ζ, which are basically functions of the points where grains touch, via a volume function $W(\zeta)$ which takes the place of the Hamiltonian and the condition $E = H$ of the thermal system is replaced by $V = W$ of the granular system. This system is said to be "jammed". The function $\Theta(\zeta)$ insures that all grains are in locked positions by touching their neighbours. An explicit definition of $\Theta(\zeta)$ is possible in 1-D [1] but its generalization to higher dimension is difficult. The transition from microcanonical to canonical ensemble in statistical mechanics is made by the introduction of temperature (2) and free energy

$$F = E - TS\,, \tag{6}$$

where

$$e^{-\frac{F}{kT}} = \int e^{-\frac{H(p,q)}{kT}}\, \mathcal{D}p\, \mathcal{D}q\,. \tag{7}$$

For jammed configurations we find $S(N,V)$ from (5), and so we define a canonical ensemble via Y which we call the effective volume, the analogue of free energy:

$$Y = V - XS = V + X\frac{\partial Y}{\partial X} \tag{8}$$

where

$$e^{-\frac{Y}{X}} = \int e^{-\frac{W(\zeta)}{X}}\, \Theta(\zeta)\, \mathcal{D}\zeta\,. \tag{9}$$

In general there are configurations of the powder which will not be described by this ensemble, for example arched holes with "rattlers" (i.e. free grains which are not in a stable contact with their nearest neighbours) in them. Nevertheless, the fruitful area for commencing study is when (5) applies and we confine ourselves to such a case.

It has been shown that external vibrations lead to a slow approach of the packing density to a final steady-state value. Depending on the initial conditions and the magnitude of the vibration acceleration, the system can either reversibly move between steady-state densities or can become irreversibly trapped into metastable states; that is the rate of compaction and

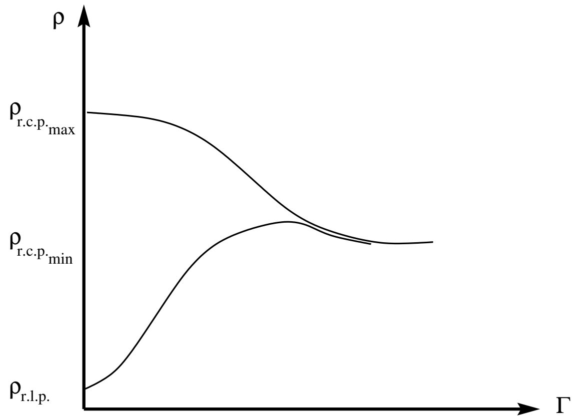

Figure 2: Dependence of the packing fraction on the history of tapping amplitude. The parameter $\Gamma = \frac{A}{g}$ is the ratio of the recorded peak acceleration during a single tap A to the gravitational acceleration g. In the Chicago experiments, Γ was varied by changing the amplitude of excitation A at fixed frequency $\omega = 30$ Hz.

the final density depend sensitively on the history of vibration intensities that the system experiences (see Figure 2). It is well known that a system of randomly packed monodisperse hard spheres has packing fraction in the range 0.64 to 0.55. The grains are poured into the tube and have a low initial packing fraction of $\rho_{r.l.p} \simeq 0.55$ which depends on the sample deposition method. Vertical vibrations are then applied in the form of individual shaking events ("taps"). Each tap consists of one complete cycle of a sine wave of the fixed frequency $\omega = 30$ Hz. The tapping intensity is parameterized by $\Gamma = \frac{A}{g}$ i.e. the ratio of the recorded peak acceleration during a single tap A to the gravitational acceleration g. Individual taps are spaced spaced sufficiently far apart in time so that the system comes to complete rest between taps and any spurious effects from continuous vibrations are absent. Further increase in Γ moves the system to a plateau at $\rho_{r.c.p_{min}} \simeq 0.61$ and this compaction is *irreversible* until the characteristic acceleration Γ^* (whose numerical value depends on the number of taps) is reached. Once a characteristic acceleration Γ^* has been exceeded, decreasing Γ, always at a fixed number of taps, takes one to the *reversible* branch with the maximum value at $\rho_{r.c.p_{max}} \simeq 0.64$. The same kind of reversible behaviour has been observed for packings of monodisperse rods though the prolate, anisotropic particle shape favours the transition from a random isotropic to an aligned ordered packing [4]. We claim that point $\rho_{r.c.p_{max}}$ corresponds to the value of compactivity $X = 0$, the point $\rho_{r.c.p_{min}}$ corresponds to $X = \infty$, and the lower curve cannot be described by equilibrium formulae of type (5) but requires transport theory (see for details Ref. [7, 8]). We argue that despite the above-mentioned difficulties it is possible in principle to construct an analogue of thermodynamics for jammed states in dense granular packings. One may argue that shape and other surface properties of grains in a powder are certainly crucial for forming a jammed configuration, but we will show that progress is already made by looking at the case of the collection of infinitely hard grains whose contact points are specified. At a cruder level several simple models of volume function have been proposed for analyzing "phase" changes in packings of spherical, elongated and irregular (i.e. strongly non-spherical) grains [6]. We have argued that the physics of rough hard powders are resolved by formula (5), but given that one is looking for an analytical "first-principles" formalism, what is W? Let us consider the simplest example of the W function, an analogue of Curie-Weiss-Bragg-Williams approximation in the statistical mechanics of alloys. Each grain has neighbours touching it with a certain coordination and angular direction. If a grain can take positions within the first coordination shell leading to contributions v_1, v_2 to the total volume, $v_1 < v_2$, packing fraction $\rho_{r.c.p_{max}}$ corresponds to the volume $V = Nv_1$,

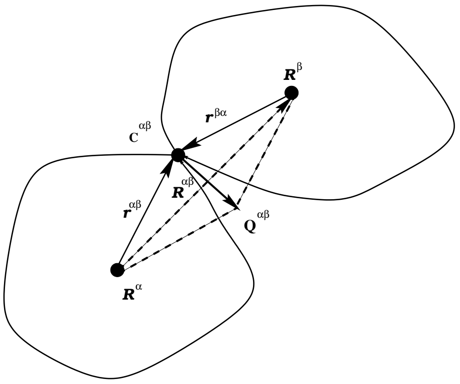

Figure 3: The centroids of two neighbouring grains in contact

and $\rho_{r.c.p_{min}}$ to $V = \frac{N(v_1+v_2)}{2}$. There is no way in which $V = Nv_2$ can arise from (9). This is of course a very crude model, but it illustrates the point. The reversible curve is a very small part of possible granular experiments, just as is the case in thermal equilibrium, but it is the basis of the *physics* of powders. Can one think of a better model? Suppose that the local characteristics of the jammed granular packing are given. Then we have to be able to calculate its volume V by expressing the volume function W in terms of the grain variables. The contact points are the total specification for static packings, thus their set must define W. How can one analytically express the volume function in terms of contact points positions? Thus W is $W(\vec{C}^{\alpha\beta})$ where $\vec{C}^{\alpha\beta}$ is the point where grain α touches grain β. Let us define the centroid of contacts of grain α (see Figure 3)

$$\vec{R}^{\alpha} = \frac{\sum_{\beta} \vec{C}^{\alpha\beta}}{z^{\alpha}}, \tag{10}$$

where z^{α} is the coordination number of grain α. We introduce the configuration tensor F_{ij}^{α}

$$F_{ij}^{\alpha} = \sum_{\beta} (R_i^{\alpha} - R_i^{\beta})(R_j^{\alpha} - R_j^{\beta}) = \sum_{\beta} R_i^{\alpha\beta} R_j^{\alpha\beta}, \tag{11}$$

with β are the nearest neighbours. One can see from Figure 3 that vector $\vec{R}^{\alpha\beta}$ joins the centroids of contact of grains α and β. Since tensor F_{ij}^{α} describes the configuration of the first coordination shell of a reference grain α, its invariants play a special role in our formalism. The determinant of this tensor is related to the volume of the first coordination shell of grain α. The volume (area in 2-d) of a jammed packing corresponding to a state on the reversible branch is approximately given by summing the volumes of the first coordination shell over the system

$$W = \sum_{\alpha}^{N} \sqrt{\mathrm{Det} F_{ij}^{\alpha}}\,. \tag{12}$$

If one considers disordered jammed configurations and ignores for the sake of simplicity many-body correlations within the first coordination shell and between those of neighbouring grains, the volume function written in terms of the configuration tensor determinant is a reasonable first approximation. One gets into problems here that are reminiscent of cluster expansions but there is a healthier status to first approximations. The addition of terms describing the correlation between coordination shells, to the volume function, makes the integration of (9) very difficult to accomplish. Given that the volume function can be written in terms of the eigenvalues of F_{ij}^{α}, one can immediately see that integration with respect to $\mathcal{D}\zeta$ actually implies integration in the space of eigenvalues. We argue that the function $\Theta(\zeta)$ can be

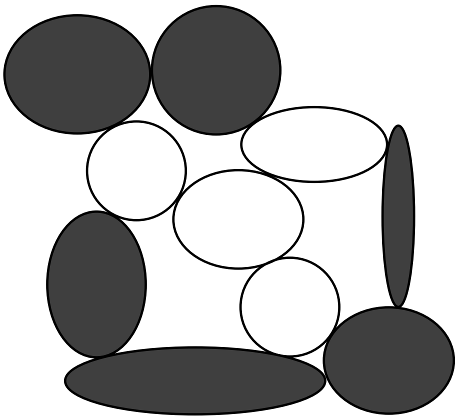

Figure 4: First coordination shell of a reference grain in the "fixed" cage of second nearest neighbours

written in terms of the second invariant of F^{α}_{ij}, i.e. its trace so that it provides the limits of integration in (9). The trace of the configuration tensor F^{α}_{ij} is

$$\mathrm{Tr}\{F^{\alpha}_{ij}\} = \sum_{\beta} |\vec{R}^{\alpha\beta}|^{2}\,, \tag{13}$$

so that $\mathrm{Tr}\{F^{\alpha}_{ij}\}/z^{\alpha}$ gives the square of an average distance between the centroids of contact within the first coordination shell of grain α. The distance between the centroids of contact of grains in contact has upper and lower bounds because particles are impenetrable and are "jammed" in the cage formed by their nearest neighbours. It is easy to see then that the presence of a step-function $\Theta(F^{\alpha}_{ii})$ insures that in a packing of hard grains in contact configurations which contain overlapping and "rattling" particles are indeed forbidden. Let us offer the following argument in support of the compactivity concept for granular packings. We argue that when a perturbation is inflicted on system e.g. with the tapping amplitude Γ and frequency ω there is a threshold for disturbance which will have domains of disturbance. The overall volume does not change, for the shaded region defies disturbance (see Figure 4). Suppose one associated a volume function W^{α} with the configuration a of the first coordination shell. Then W^{α} is conserved when the particular perturbation is imposed, but the actual configuration is changed to $\tilde{W}^{\alpha}$ and the packing volume $W = \sum_{\alpha} W^{\alpha}$ is unchanged so it can be expressed as the conservation law

$$\sum_{\alpha} W^{\alpha} = \sum_{\alpha} \tilde{W}^{\alpha} \tag{14}$$

Suppose configuration is defined by the probability $f^{a}(W^{\alpha})$ of finding a configuration W^{α} so that one construct a Boltzmann equation

$$\frac{\partial f^{a}}{\partial t} = \int K\Big(\prod f^{a} - \prod \tilde{f}^{a}\Big) \tag{15}$$

where the kernel K depends on Γ and ω. The kernel K contains $\delta\Big(W_{a} - \tilde{W}_{a}\Big)$ hence the solution must be $f^{a} = e^{\frac{Y-W^{\alpha}}{X}}$. This can be applied to the whole packing of volume V considered as a set of domains whose stability threshold is breached and which rearrange under the perturbation. The steady-state is then determined by the probability distribution $P = e^{\frac{Y-\sum_{\alpha} W^{\alpha}}{X}}$ and $X = X(\Gamma, \omega)$ which provides one with an analogue of the Einstein relation [7].

3 CONDUCTIVITY MEASUREMENTS

The conductivity is dependent on both the packing fraction, ρ , and the average coordination number, $\bar{z}$, and both change little over the reversible and irreversible regimes. From this one might conclude that the relationship between the volume fraction and the conductivity is not very far from linear. They are related to the effective scalar conductivity, k^*, by:

$$\frac{k^*}{k} \propto \frac{1}{2}\rho\,\bar{z}\,, \tag{16}$$

where k is the scalar conductivity. Hence, given the that the conductivity depends on the product of two unknown variables, a second expression relating conductivity to either the coordination number or the packing fraction must also be found, so that a direct relationship can be made between conductivity and packing density. Therefore, a relationship between packing density and conductivity is not straightforward. However, the packing density can be obtained experimentally from capacitance or conductivity. A common method employed to measure packing density is to calibrate density measurements by measuring the height of grains in a tall, thin tube with capacitance, and then to directly measure the capacitance of the tube during experiment where the tube is subjected to vibrations [2, 3]. However, there are problems with measuring capacitance. The permittivity of air is as much as 0.5 of that of glass beads. Capacitance techniques also require very sensitive equipment and a trade-off between sensitivity and temporal resolution has to be made. A much simpler technique is to measure the conductivity of conducting particles. The technique is essentially identical, but the main difference is that the conductivity of air is a very small fraction of conducting particles, so there is no need for a trade-off between sensitivity and temporal resolution.

Let us present a brief description of the experimental setup and measurement technique. Packings composed of graphite (gas-carbon) grains of irregular shape (see Figure 5) were confined to a glass tube of diameter $15mm$ and length $70mm$. It was then necessary to confirm that the coefficient of friction was independent of size. This was established by making use of the measurement of the bulk friction coefficient of each size of grain by the Coulomb method, where the coefficient is equal to the tan , where θ is the angle of inclination of a pile of grains poured onto a flat, horizontal surface. This was measured to be $43 \pm 1^\circ$ meaning the coefficient of friction was 0.93 ± 0.3 and was independent of grain size. Using the method of sequential deposition we prepared four different polydisperse packings with grain sizes within the range of 150-212, 212-300, 300-425 and 425-600 μm. It was clear from an examination of the gas carbon grains after the experiments had been carried out, that very fine grains of material had broken off the large grains of gas carbon. This made a fine dust.

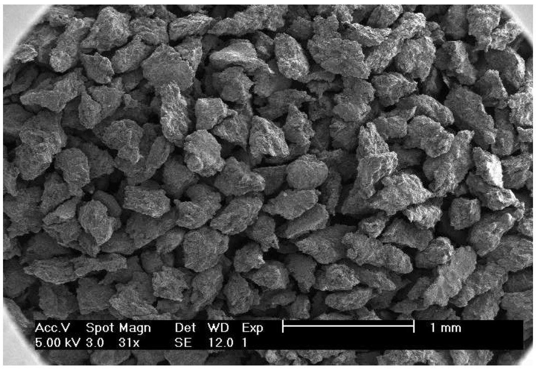

Figure 5: Electron microscope image of carbon grains after the tapping experiment. The surface properties, average grain size and polydispersity remain unchanged by the vibration procedure.

However, the quantity of this dust was small, and would not have had a significant effect on the outcome of the results. We also used packings of irregularly shaped, polydisperse, with sizes ranging from 100 to 500 μm and aspect ratios varying between 1 and 5, iron filings (see Figure 6) as a reference sample since these grains have much greater electrical resistance. The problem with these particles was that whilst iron filings did conduct, they quickly oxidized, reducing their conductivity.

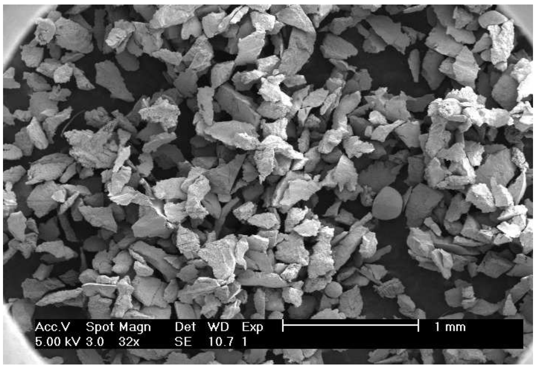

Figure 6: EM image of iron grains after the tapping experiment. The surface properties, average grain size and polydispersity remain unchanged by the vibration procedure.

A loudspeaker was connected in series with a signal generator. Connected to the diaphragm of the speaker was a glass tube containing conducting granular material and two carbon rods acting as electrodes of equal height glued to the inside-edge of the tube, directly opposite each other. These were connected in series with a power supply, a variable resistor and an analogue data recorder. The current (proportional to the conductivity) and voltage through the sample was measured by the data recorder. The input to the speaker, and the response waveform in the current through the granules, found by measuring the voltage across the resistor, was read with an oscilloscope. Experiments were carried out with an input signal applied to the loudspeaker. This was a square wave of step width 1 ms and frequency 7 Hz. The height of the square wave input was ramped up and down with a fixed number of taps at 0.5 V intervals. This converted to accelerations of magnitude approximately 1.5 ms^2. The increase in voltage was halted when the conductivity in the response form reached zero on the application of the tap. This was carried out for various numbers of taps per increment and the results measured. A problem with the waveform was that there were two accelerations per tap, in the up part of the pulse and the down part of the pulse. In the down part of the pulse, the acceleration had no affect on the conductivity of the granules. It was equivalent to tossing a pancake by moving the pan downwards first. Instead, the best course of action was to restrict the acceleration to a single one in the up direction, using a saw-tooth curve. The saw-tooth waveform was achieved with a standard relay circuit with a resistor and capacitor in parallel. The length of the down-slope was varied by varying the magnitude of the capacitor, the length of the up-slope altered by altering the value of an inductor connected in series.

The first experiments were carried out with the input signal a square wave (duration 10 ms) as the input pulse to the loudspeaker. The conductivity of the sample, containing conducting iron filings (see Figure 6), was directly measured with the data recorder and for the first time the exact nature of how a granular material responds to excitation is reported here. The advantage of measuring the conductivity of the sample, rather than the capacitance, is that the instantaneous change in conductivity can be directly measured in this way with relative ease. Using iron filings, and the same pulse conditions as before, the voltage applied to the loudspeaker was ramped up and down several times, but this time at 100 taps, and

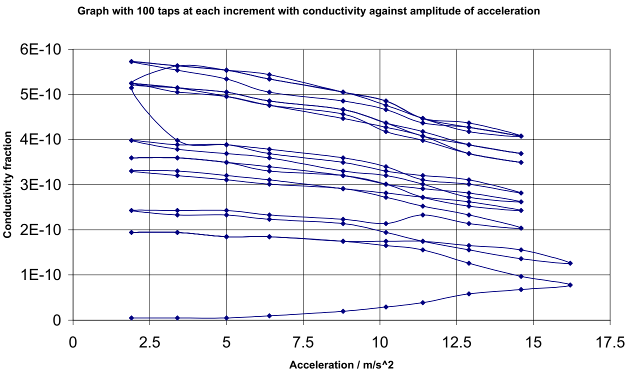

Figure 7: Conductivity fraction at various stages during the tapping experiment in which the packing of iron filings was vibrated for 10^2 taps at each value of the acceleration amplitude as it was ramped from 2 to 14 and back for several cycles in steps corresponding to 0.5 V.

1000 taps per increment of amplitude. It is clear that at these points, the system has not yet come to equilibrium before the vibration amplitude is altered. This experiment was designed to give an indication of how a granular medium behaves whilst not in equilibrium and the results for both these experiments are shown in Figures 7 and 8. From the graphs, it is clear that the curves still exhibit the same characteristic shape as when the granules reach equilibrium. However, the granules have not reached the maximum packing density before the acceleration amplitude is altered. Consequently, the first sweep of all the accelerations produces a curve squashed in the conductivity (y-axis) direction. A suitable analogy for this behaviour is found in glasses which are out-of-equilibrium systems. A good way to consider what is happening is by use of ramping rates. Firstly, the faster that the acceleration is

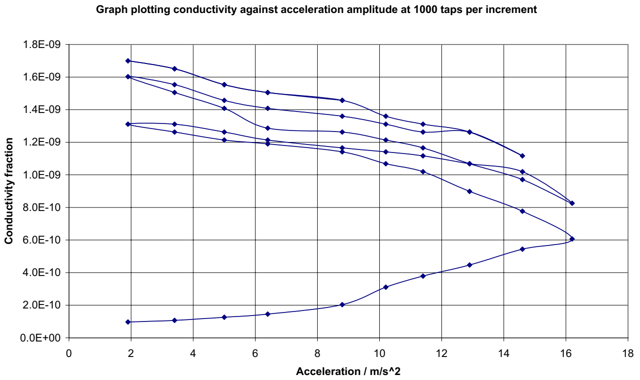

Figure 8: Conductivity fraction at various stages during the tapping experiment in which the packing of iron filings was vibrated for 10^3 taps at each value of the acceleration amplitude. The reversible branch is reached after only 2 cycles.

ramped up, the further the system will settle from equilibrium. In glasses, a fast cooling rate has the same effect. Continued vibrations of the medium encourages the granules to approach equilibrium more closely. This compares with annealing mechanisms in glasses. Finally, as can be seen in Figure 7, there is a large gap in the readings when a ramping cycle had been completed. Here, the system was left to sit for an hour. After that hour had passed, the conductivity had increased slightly. This appears to be analogous to creep in glasses.

Whilst iron filings did conduct, they quickly oxidized, reducing their conductivity. It was also difficult to sort their size, as they had a high aspect ratio. Gas-carbon rods were ground up into sub-millimetre particles and used instead. Again, a square wave of pulse duration 10 ms and repetition frequency 7 Hz was used as the input. The amplitude of the square wave input was ramped up and down with a fixed number of taps at half volt intervals. The intervals were correlated with measurements taken with a high-speed camera to calibrate the voltage with the real acceleration of the particles. The increase in voltage was halted when the conductivity in the response trace reached zero on the application of the tap: i.e. all particles lost contact. This converted to accelerations of approximately 1.5 g. The experiment was carried out with 2000 taps per increment, empirically determined to be the point where the conductivity approximately attains the maximum conductivity at a certain increment. The results showed what was largely expected. The grains exhibited a similar conductivity profile, to the density profile reported by Chicago et al. [2, 3], and the reversible regime on the graph was independent of particle size - the reversible regimes could all be superposed, as shown in Figure 9. Using irregular grains and conductivity to measure packing density exhibits the same characteristics as spherical grains using a capacitance measuring method.

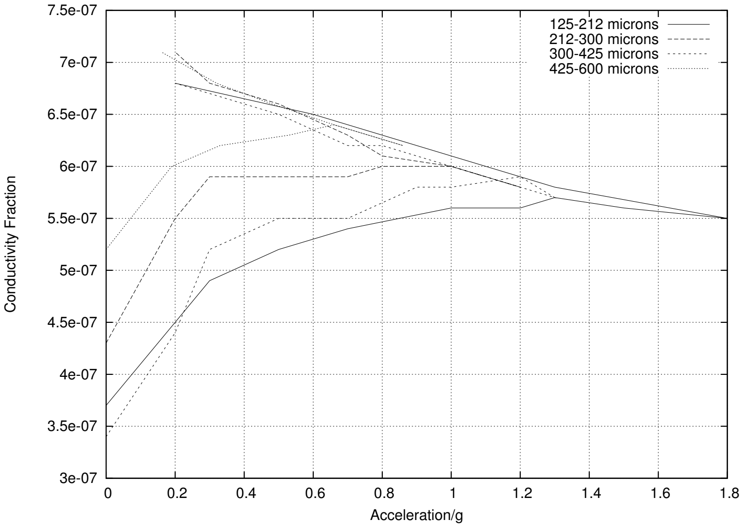

Figure 9: Normalised conductivity fraction as a function of the dimensionless acceleration amplitude for grains of different sizes. The packings were prepared in a low packing fraction state by sequential deposition. The acceleration amplitude was first slowly increased and then decreased. The conductivity fraction was recorded after 10^5 taps at each value of the acceleration amplitude. The lower branches are irreversible and depend on the deposition history and particle size. The upper branches for grains of different sizes are reversible i.e. upon subsequently raising the value of the acceleration amplitude again, the conductivity fraction retraces the values measured on the downward trajectory.

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