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Random Close Packing of Granular Matter

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Abstract We propose an interpretation of the random close packing of granular materials as a phase transition, and discuss the possibility of experimental verification.

Keywords Granular matter · Random close packing · Phase transition

1 Introduction

Static granular matter, such as sand, exhibits several properties which distinguish it from matter in thermal equilibrium; see [6] for a review. One property which has been studied since introduced by Reynolds in the 1890's is that of dilatancy [16]. Another property is random close packing [22], which has received attention periodically since the 1960's. We will return to dilatancy below; this paper is mainly concerned with random close packing.

The phenomenon of random close packing was popularized by Bernal [2] as part of his effort to model liquids. The experiments which clarified many of the issues were performed by Scott *et al.* [19, 20, 22], and showed the following. If a large number of monodisperse hard spheres, for instance steel ball bearings, are gently poured into a container, their volume fraction will be roughly 0.61. If the container is repeatedly shaken vertically, this density rises to about 0.64, and careful protocols lead to reproducible lower and upper limits on the volume fraction, called, respectively, random loose packing (0.608 ± 0.006) and random close packing (0.6366 ± 0.0005) [22]. Note the small error bars for the density of random close packing.

Random close packing is usually associated with samples produced by shaking. However, Scott *et al.* noted already in 1964 [20] that volume fractions beyond 0.64 (up to approximately 0.66) could be obtained if the material was cyclically sheared, and that this result was accompanied by small crystal-like clusters of spheres. This was confirmed and explored by Pouliquen *et al.* [13] (who also performed experiments employing horizontal

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shaking [15]), obtaining volume fractions up to 0.70, again accompanied by crystal-like clusters of spheres. (Recall that the densest possible packing of monodisperse spheres has volume fraction $\pi/\sqrt{18} \approx 0.74$.)

In light of the above the volume fraction 0.64 is generally described as the boundary between two regimes for granular matter: at volume fractions below 0.64 the structure of the material is random, while above 0.64 it has some order, as represented by the crystal-like clusters which appear. This can be rephrased by saying that 0.64 is the highest density at which the spheres are randomly distributed. However, now taking into account the possibility of also approaching 0.64 from above one must revisit the small error bars on the density of random close packing quoted above from [22]. This will be important in what follows.

Granular matter under shear stress collapses if it is loosely packed, while it expands if sheared when densely packed—this is the phenomenon of dilatancy—and in the soil mechanics literature the density dividing the two regimes is called the critical state density [12], a volume fraction of about 0.6. However there are no tables of the critical state densities for various preparations of granular matter in the way there are tables for properties of equilibrium matter. We note the parallel between dilatancy and the phenomenon of random close packing, which is also not well understood. In fact in an influential paper Torquato *et al.* [24] claim to "have shown that the notion of RCP (random close packing) is not well defined mathematically". What they are questioning is whether there could *possibly* be small error bars as the purported density of random close packing is approached (from above), as the desired quantity is potentially dependent on protocols. Their arguments are based on computer simulations, not physical experiments. Indeed, there have not been physical experiments at volume fractions just above volume fraction 0.64, reported in the literature, with the precision of those performed by Scott *et al.* at volume fractions below 0.64.

One difficulty in classifying the properties of granular matter arises from memory effects. For instance it is known that the pressure distribution at the bottom of a sand pile will be different if the pile is deposited from a stationary narrow funnel than if it is deposited more uniformly [6, 25]; in this sense static granular matter is analogous to glassy solids. However, using careful preparation protocols progress has been made on understanding dilatancy by the recent experiment [23] which showed that the critical state density is the transition point between two well defined phases of the material. (More precisely, one feature of the phase transition is a discontinuity in the *rate of change* of the volume response of the material to shear; it is not yet known if the *sign* of the volume response changes at the same density.) This means that appropriate preparation should be able to make the error bars in the critical state density of a specific granular material as small as desired. In this paper we propose a similar sharp interpretation of random close packing, namely as another phase transition point of the material. We discuss a mathematical model and an experimental test of our interpretation.

2 Analysis

Our proposed characterization of random close packing is motivated by properties of the hard sphere model of classical equilibrium statistical mechanics. In that model point particles, with the usual position and momentum degrees of freedom, interact only through a hard core: no pair may approach closer than some fixed separation D, and the particles evolve dynamically through elastic collisions of imaginary spheres of diameter D surrounding their positions. Our interest in the hard sphere model stems from the demonstration by Alder and Wainright [1], by molecular dynamics simulations, that the model exhibits a first order phase transition between a fluid, which exists at volume fractions below 0.494 ± 0.002, and a solid,

believed to be crystalline, which exists at volume fractions above 0.545 ± 0.002 [9]. Between 0.49 and 0.54 there is a mixed phase. Using the canonical ensemble we integrate out the momentum variables and consider the "reduced" probability distributions on the phase space of the position variables alone, in the infinite volume limit. They are the infinite volume limits of the uniform distributions on packings for fixed volume fraction. In particular the distribution $p(m)_\phi$ of the mixed phase at volume fraction ϕ, $0.49 \leq \phi \leq 0.54$, is represented by an average of the distributions of the pure phases: $p(m)_\phi = c\, p_{0.54} + (1-c)\, p_{0.49}$, where $p_{0.49}$ is the distribution of the highest density fluid, $p_{0.54}$ is the distribution of the lowest density solid, and $0 \leq c \leq 1$ is such that $p(m)_\phi$ corresponds to volume fraction ϕ. (This is merely a statement of the fact that distinct phases separate when coexisting in equilibrium, each occupying a well defined volume [11]. We discuss this further below. The distribution $p(m)_\phi$ is for the infinite system, and its form means that the fraction c of samples would represent an infinite system at volume fraction 0.54 and a fraction $1-c$ of samples would represent an infinite system at volume fraction 0.49; the value $c = (\phi - 0.49)/0.05$ then gives the average volume fraction ϕ for $p(m)_\phi$.) Note that 0.49 is the volume fraction of "freezing". Therefore assuming, as generally believed, that the solid phase is crystalline (in fact face centered cubic [3, 26]), we interpret 0.49 as the "highest random density" among monodisperse spheres. (These structural features have been confirmed not only by many computer simulations but also in experiments with appropriate colloids [17].) Intuitively, at any volume fraction above the freezing point there is a nonzero probability of (seeing) an infinite, ordered crystal. It is the use of the infinite volume limit, together with the probabilistic formalism, which produces a sharp phase transition between disorder and order in equilibrium statistical mechanics [8].

We emphasize that there are sphere packings with volume fraction $\phi > 0.49$ which might well be described as random, for instance packings corresponding to any metastable extension of the fluid branch of an isotherm. However the total of all such packings has probability zero with respect to the (infinite volume limit of the) uniform distribution on packings with volume fraction ϕ. Our use of this distribution as the touchstone of relevancy is in accord with its common appearance in statistical physics and probability theory; the best justification one can give is that it is commonly found that practical sampling of phase space seems to occur in this way, in particular in the natural dynamics of matter in thermal equilibrium. Any computer simulation purporting to model the behavior of "hard sphere" colloids should reflect this probability distribution and should therefore see the emergence of order at volume fraction 0.49, if enough precision were available.

In summary, the hard sphere model, and its physical realization in colloids, exhibits the basic ingredients needed to make sense of the granular phenomenon of random close packing: in the hard sphere model there is a precise volume fraction, roughly 0.49, which separates the fluid phase of random packings from the mixed phase in which crystalline order begins to appear. This defines a highest density in which the packings are random, with, in principle, arbitrary precision. While this is not directly applicable to the granular matter which is our proper subject, it nonetheless shows that the intuitive notion of random close packing is not inherently inconsistent as claimed in [24].

We now turn to granular matter. The traditional hard sphere model does not include the effects of gravity and cannot represent the properties of granular matter, in particular that of random close packing. However a slightly modified ensemble framework has been proposed as a model for granular matter. Specifically, in the original proposal of Edwards *et al.* [7] one uses a uniform distribution on those static monodisperse sphere packings, of fixed volume fraction, which are mechanically stable under gravity. One can add friction to the spheres and perhaps other restrictions besides volume fraction; adding a condition of fixed pressure

might be useful, though it is not clear if pressure is isotropic in granular materials. We expect that this model would show a first order phase transition analogous to the liquid/solid transition in the hard sphere model, though we have no evidence of this. But it is this use of probabilistic reasoning that will allow us to avoid the problems discussed in [24].

Historically, our understanding of the hard sphere situation is based primarily on molecular dynamics and monte carlo simulations. There is still no analytic proof of a phase transition in that model (see however [4, 5]), and the experimental confirmation [17] is relatively recent since the model is not a good fit to naturally occurring molecular or colloidal systems. For granular materials we expect physical experiment to be the easiest path to pursue; both analytic and simulation approaches are probably harder than for the hard sphere model, while there is an abundance of naturally occurring (noncohesive, hard) granular systems.

As is true for solids in thermal equilibrium, in order that an ensemble method be appropriate for (*nonequilibrium*) granular matter it is important to restrict the protocols used to produce beds of granular matter at fixed volume fraction (and perhaps pressure etc.). One feature that is necessary is that the protocol be "history independent" [14] in that it give equivalent results starting with beds originally prepared in any manner. There are three types of protocols which claim to produce history independent beds of monodisperse granules with well defined volume fractions: vertical vibration (often called "tapping"); fluidization followed by sedimentation; and cyclic shearing. These methods have produced history independent beds with volume fractions in the following ranges: 0.605 to 0.625 by vertical vibration [14, 18]; 0.685 to 0.70 by cyclic shearing [13]; and 0.57 to 0.62 by fluidization/sedimentation [21, 23].

As noted above, it is known from Schröter *et al.* [23] that granular beds prepared by fluidization/sedimentation undergo a phase transition, as volume fraction is varied, at approximately 0.60 volume fraction, as measured by two different responses to shear. Given the mathematical similarity between the hard sphere model and the granular model of Edwards on the one hand, and the experimental similarity between the sharp freezing transition in colloids [17] and the abrupt appearance of crystalline clusters in the experiments of Scott *et al.* [20] and of Pouliquen *et al.* [13] on the other hand, we conjecture that history independent granular beds would show another phase transition: a first order phase transition, with a mixed phase for volume fractions between 0.64 and 0.74, again exhibited through the response to shear or other mechanical probe. By analogy with the hard sphere model the distribution for granular matter in the mixed phase would be a mixture of a crystalline state at volume fraction 0.74 and a disordered state at volume fraction 0.64. This would give a well defined meaning to the phenomenon of random close packing of granular matter just as the freezing density defines a similar concept for the hard sphere model or for hard sphere colloids. In Figs. 1 and 2 we contrast the (reduced) entropy in the hard sphere model with our conjecture of the entropy in the Edwards model. The flat portions of these convex graphs represent coexistence regions of first order transitions, as usual in thermodynamics; to say that the state in the coexistence region is a convex combination of the states (*i.e.* probability distributions) at the edges of the region is a generalization from entropy to all observables, as usual in statistical mechanics.

We note the connection between this proposal and that of Kamien and Liu [10], which also uses the hard sphere model to understand random close packing. In [10] random close packing is associated with the end point of a metastable branch in the hard sphere phase diagram (see Fig. 3), while we use the hard sphere model only to conjecture behavior in a related but different ensemble, of packings which are mechanically stable under gravity, and in particular we conjecture a phase transition at volume fraction 0.64 similar to the transition at 0.494 in the hard sphere model (see Figs. 1 and 2).

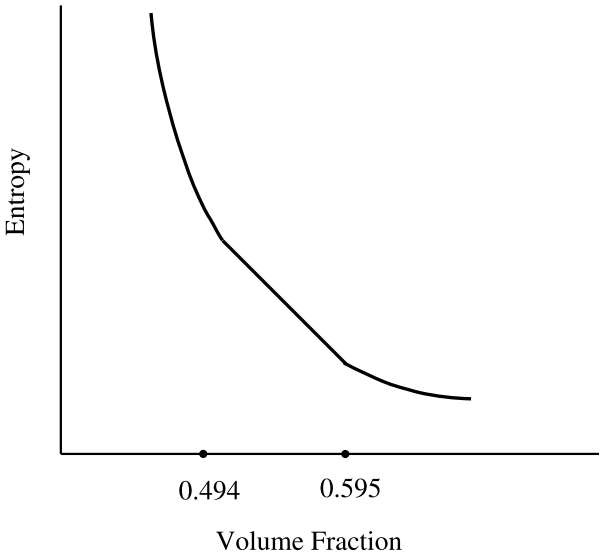

Fig. 1 The entropy in the hard sphere model

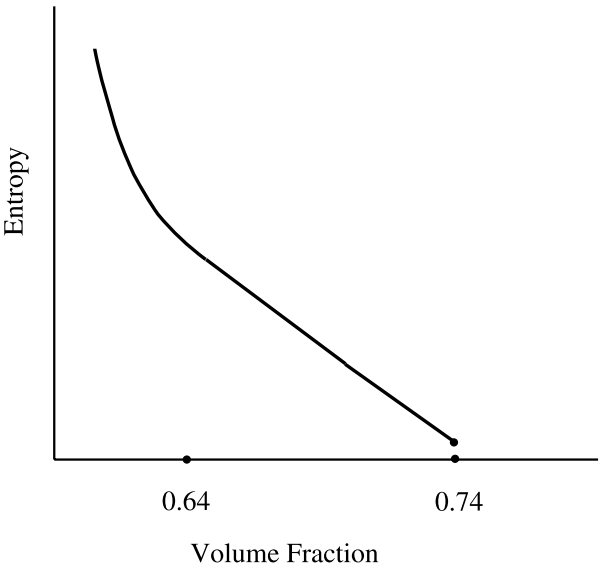

Fig. 2 The conjectured entropy in the granular model

History independent experimental protocols have not yet produced beds with volume fraction in any interval containing the volume fraction of interest, 0.64. This will be necessary before our conjecture can be checked against the behavior of granular matter, and it would seem that the method of cyclic shearing would be the best candidate for such a protocol. Alternatively it might be possible to test the conjecture by computer simulations. These should either sample the uniform probability distribution of packings at fixed volume fraction and with the mechanical stability and other restrictions noted above, or else it should accurately model the cyclic shear experiments. For both physical experiments and computer simulations we expect that rather than seek convincing evidence of a sharp transition based

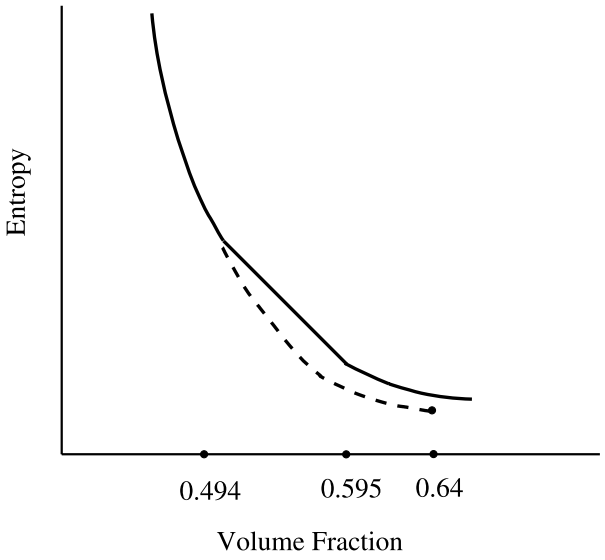

Fig. 3 A metastable branch (*dashes*) in the hard sphere model

on the sudden growth of crystals above a critical density it is more practical to look for evidence of the transition in the response of the material, as a function of the volume fraction, to some applied force, either constant as in [23] or oscillatory (acoustic). This is one of the lessons learned from the simpler hard sphere model, in which fifty years of simulations have still not shown direct evidence of crystalline symmetry even far from the coexistence region [3, 26].

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