Random close packing in a granular model

David Aristoff and Charles Radin[a]

Mathematics Department, University of Texas, Austin, Texas 78712, USA

We introduce a two-dimensional lattice model of granular matter. Using a combination of proof and simulation we demonstrate an order/disorder phase transition in the model, to which we associate the granular phenomenon of random close packing. We use Peierls contours to prove that the model is sensitive to boundary conditions at high density and Markov chain Monte Carlo simulation to show it is insensitive at low density. © *2010 American Institute of Physics.* [doi:10.1063/1.3511359]

I. INTRODUCTION

Granular materials, such as a static pile of sand sedimented in a fluid such as air or water, exhibit interesting characteristic behavior near certain volume fractions. For sand in water, the lowest possible volume fraction (called the *random loose packing density*) is about 0.57 and the highest possible volume fraction is about 0.74. In other words a sand pile can exist with volume fraction anywhere in the interval (0.57, 0.74). Within this range there are also, the *critical state density*, about 0.60, and the *random close packing density*, about 0.64.[3] We will be modeling random close packing in this paper.

Experimentally, a granular material such as sand appears quite disordered at densities below about 0.64 but inevitably contains crystalline clusters above that density, which are larger at higher densities.[11,14] This has obvious features in common with the behavior of equilibrium fluids as they begin to freeze, as noted in.[12]

On the theoretical side, there is no generally agreed model for granular materials but one candidate, usually credited to Ref. 4, uses a simple modification of the microcanonical formalism of equilibrium statistical mechanics: a uniform probability distribution on all packings of a box, by appropriate shapes, which are mechanically stable under gravity and friction. One can then try to interpret the features of granular materials in terms of "phases," using an obvious analogue of the thermodynamic limit. See Ref. 1 concerning the granular phenomenon of random loose packing and Ref. 2 for the critical state density. For random close packing such an approach was conjectured in Ref. 12, and this paper is an attempt to flesh out this conjecture with a toy model. We show in our model that at high density the system is sensitive to boundary conditions, while at low density it is not, with a perfectly sharp transition in between, in the infinite volume limit.

Our model is a variant of the old equilibrium model of hard hexagons on a triangular lattice,[7–9] with hexagonal edges larger than the lattice spacing. For such equilibrium models one can use Peierls contours to prove the existence of an order/disorder transition; the contours are used to prove sensitivity to the boundary at high density, while it is easy to show insensitivity at low density since the particles are essentially independent. In our granular model a similar high density analysis is still possible. However the low density argument is now much harder, since, as noted above, granular matter does not exist at very low densities.[3] In other words, this work is an attempt to adapt known methods of proof from equilibrium statistical mechanics to a more complicated "granular" setting, in particular to understand/model random close packing.

---

[a]Author to whom correspondence should be addressed. Electronic mail: radin@math.utexas.edu.
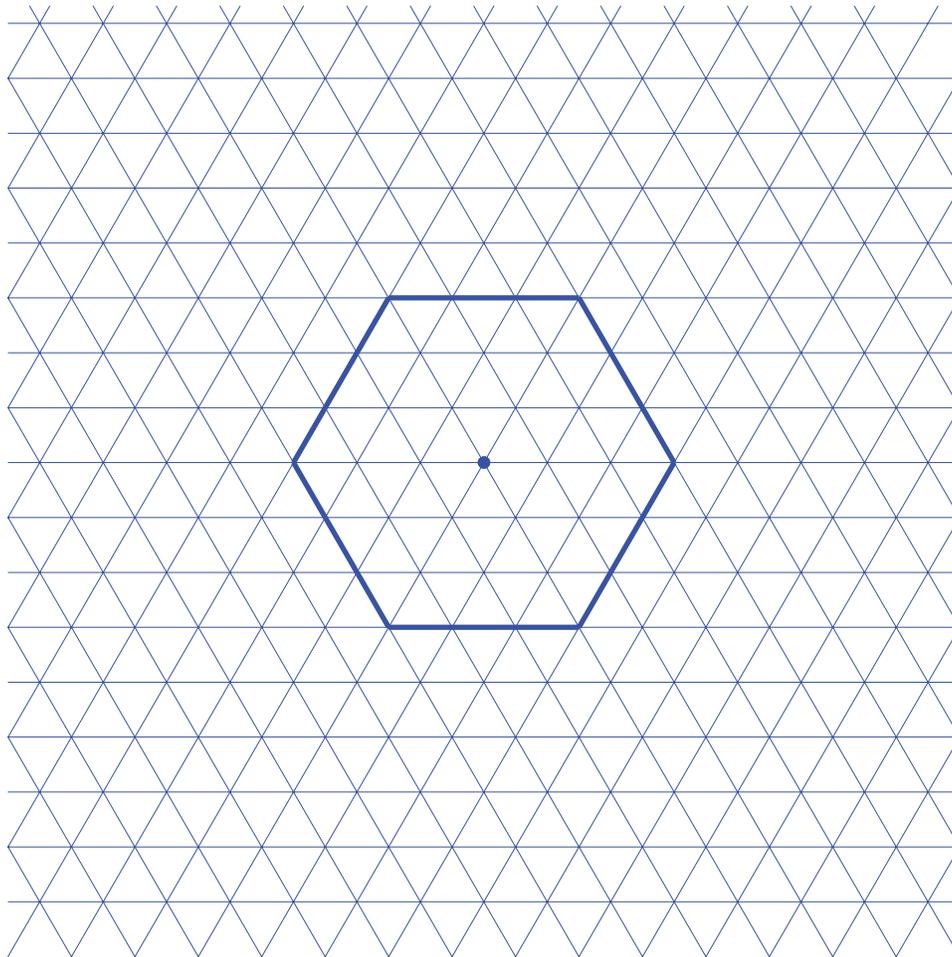
51, 113302-1

FIG. 1. (Color online) An hexagon on the triangular lattice.

II. THE MODEL AND NOTATION

Our model consists of nonoverlapping regular hexagons on a triangular lattice, with extra (granular) conditions. To mimic the effects of gravity and friction we impose the condition that each hexagon sits on top of another hexagon, that is, one of its lower edges intersects an upper edge of another hexagon. We put a probability distribution on the set of such configurations which can be thought of as a "grand canonical" version of the Edwards model[4] of granular matter noted above. In our version the probability of seeing a configuration of n particles in a fixed volume V is proportional to $e^{\mu n}$, where $\mu \in \mathbb{R}$ is a parameter controlling volume fraction.

We note that there was a previous granular adaption of the equilibrium hard hexagon model by Monasson and Pouliquen.[10] Their model differs in several important details, for instance in their use of periodic boundary conditions and their focus on thin cylindrical packings. They use their model to study entropy of granular particle packings rather than random close packing.

We consider configurations of hard-core (i.e., nonoverlapping) regular hexagons centered on a regular triangular lattice L, with side length a fixed integer multiple, s, of the lattice spacing (see Fig. 1). The hexagons are inside a square container V whose boundary is part of a tiling of the plane by hexagons (see Fig. 2). Each hexagon inside V must intersect one of the three upper edges of another hexagon.

We define a probability measure m_V on the subsets of the set of all such configurations, such that the probability of seeing a given configuration with exactly n hexagons is equal to $\exp(\mu n)/Z_V$, where μ is a variable parameter and Z_V is the appropriate normalization. Let m be any weak*limit
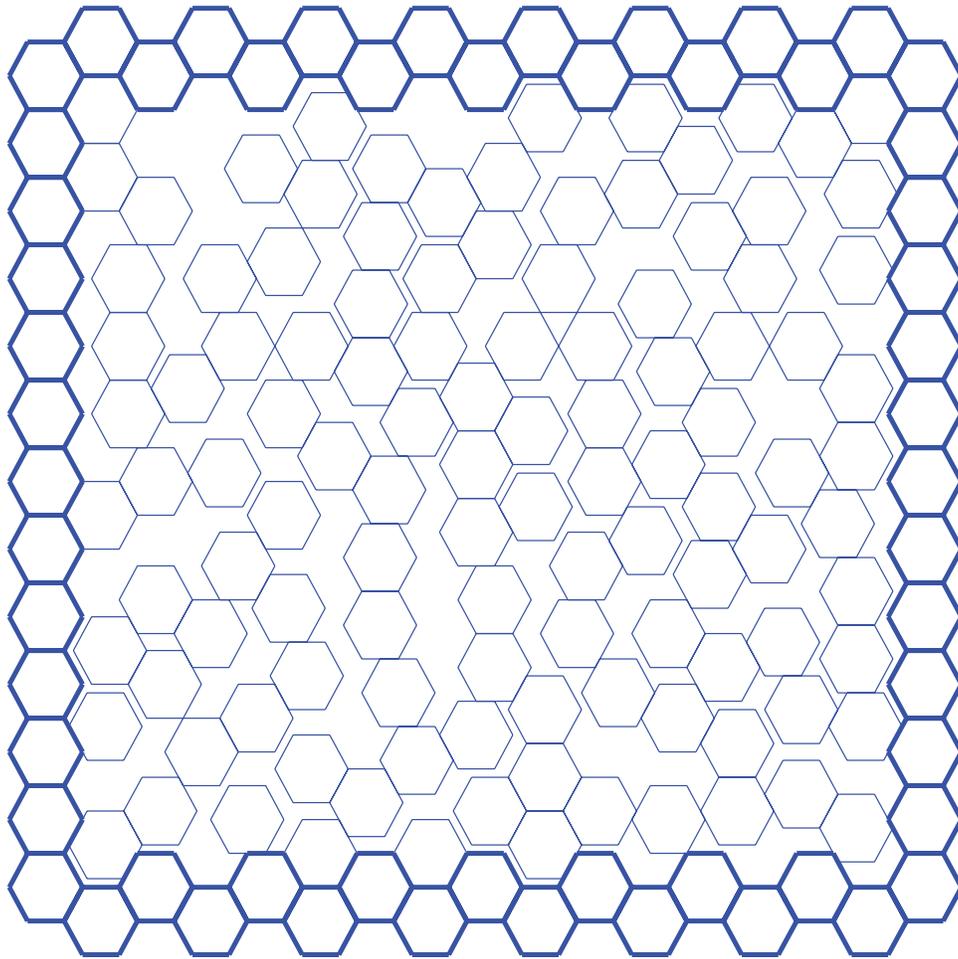
FIG. 2. (Color online) A configuration (boundary is in boldface).

point of the measures m_V, as $|V| \to \infty$. (Such limits exist by compactness. Clearly m_V and m depend on μ but we suppress this for ease of notation.)

We show that the model exhibits an order–disorder transition. At large positive μ, the measure m depends on the precise boundary conditions chosen while taking the limit $|V| \to \infty$; for a small positive μ, the measure m is unique. Thus for large μ, the center of a configuration will be sensitive to a distant boundary, while for small μ the system behaves like a disordered fluid. We prove the former statement and provide Monte Carlo simulation evidence to justify the latter.

Before giving a precise meaning to our result on sensitivity to the boundary we need a few definitions. Recall that L is the regular triangular lattice on which our hexagons are centered.

A *sublattice* is a subset of L consisting of the centers of a collection of hexagons which tile the plane. (There are $3s^2$ distinct sublattices.) We say a collection H of hexagons is *on the boundary sublattice* if the centers of all the hexagons in H are in the sublattice defined by the hexagons on the boundary of the container V.

Given a point x in the boundary sublattice, we define the *neighborhood* N_x of x to be the set of all points in L inside a hexagon h centered at x, excluding those on the bottom three edges of h.

A *contour* is a connected component of the union of the following two sets: (the closure of) the set of all space inside V not covered by hexagons and the set of all line segments of length at most $s - 1$ which are intersections of neighboring hexagons. Given a contour C, the *region enclosed by* C is the simply-connected region of minimal area which contains C. We use the term *outer contour* for a contour which is not contained in any region enclosed by any other contour. See Fig. 3.
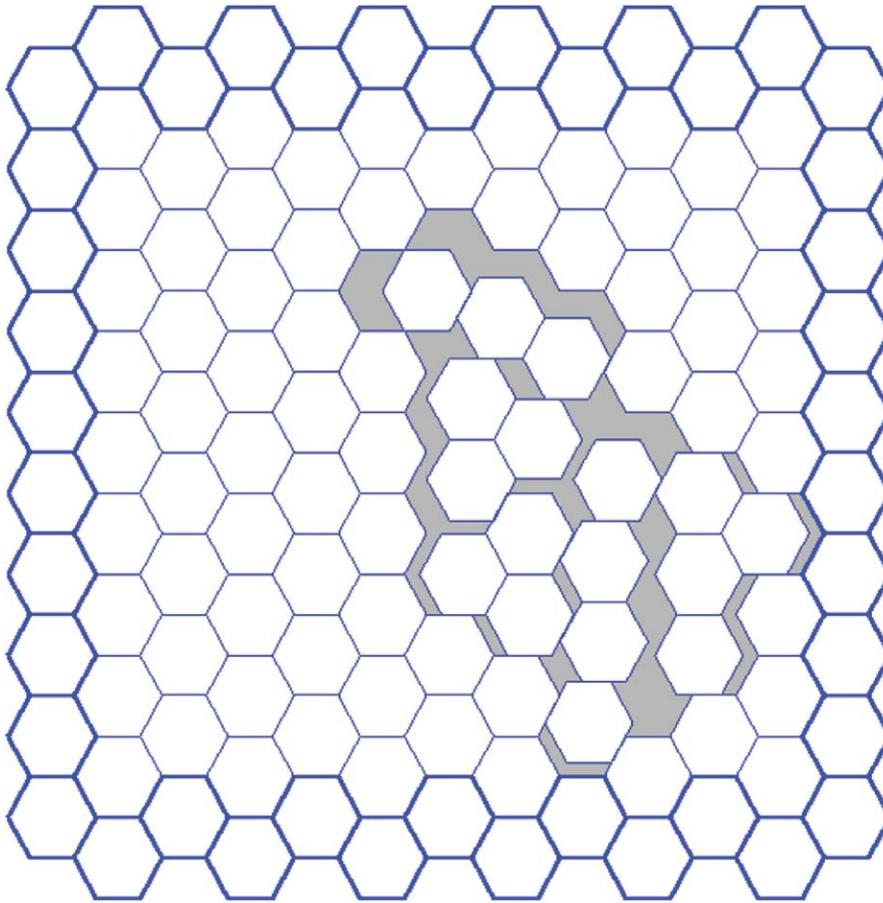
FIG. 3. (Color online) An outer contour (shaded region).

Let C be a contour of area k (in units of hexagon area), and let E be the region enclosed by C. The (closures of the) connected components of $E - C$ (the complement of C in E) will be called C-*interior regions*. Note that the hexagons which intersect the topological boundary of a C-interior region R are on the same sublattice. We say these hexagons are on the *outside* of R and we say the remaining hexagons in R are on the *inside* of R.

We assume without loss of generality that the origin O is in the boundary sublattice. We use the shorthand $p_V(\mu)$ for the m_V-probability that, given there is a hexagon h centered at a point in the neighborhood N_O of the origin, h is centered at the origin. We write $p(\mu)$ for the corresponding (infinite-volume) m-probability; we will focus on this quantity in our analysis of order.

III. HIGH DENSITY

The following is our main result on high density behavior.

Theorem 1: *For sufficiently large* μ, $p(\mu) > (3s^2)^{-1}$; *that is, a hexagon centered in* N_O *will not be centered equiprobably on each of the* $3s^2$ *sublattices.*

Note that if there is no hexagon centered in N_O, or if there is a hexagon centered in N_O, but not at the origin itself, then there is an outer contour enclosing the origin. Our proof, which begins with this observation, relies on the following two main ingredients: first, we must show that the probability of seeing a fixed outer contour C becomes exponentially unlikely as the area of C increases; second, we put an exponential upper bound on the number of contours of fixed area enclosing the origin.
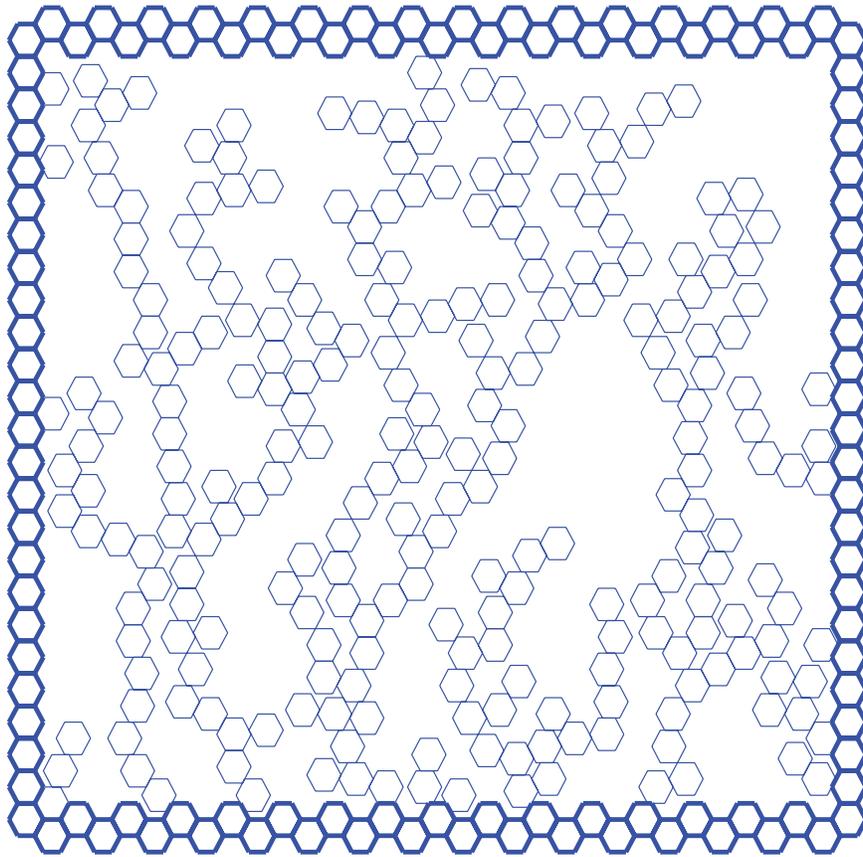
FIG. 4. (Color online) A configuration of 250 hexagons in equilibrium at $\mu = -4$, in a system of volume 729.

The first estimate can be improved by taking μ large and then by combining both ingredients one obtains the theorem.

Lemma 1: Let C be an outer contour of area k (in units of hexagon area). The m_V-probability that a configuration has the contour C is at most $\exp(-\mu k)$. *This estimate is independent of V.*

Proof: The main idea of the proof is to create a $1-1$ correspondence between configurations having the contour C and configurations without C but with more hexagons, since for positive μ the latter will be exponentially more likely. Going in this direction, we define a $1-1$ correspondence $\mathcal{S} \to \mathcal{T}$, where

(a) $\mathcal{S} = \{$configurations in V with the contour C and n hexagons$\}$,
(b) $\mathcal{T} = \{$configurations in V with $n+k$ hexagons$\}$,

as follows. Let $A \in \mathcal{S}$. We define a map $A \to A'$ as follows. For each C-interior region R of A, pick a hexagon h on the outside of R, without loss of generality h is centered at $x \in N_y$, and translate R by $y - x$ while leaving the rest of A unchanged. This produces a unique arrangement A' of hexagons in V. We show that the hexagons in A' are nonoverlapping and furthermore that A' has a void C' which can be covered by k nonoverlapping hexagons.

Suppose h_1 and h_2 are distinct hexagons in A, and let h_1' and h_2' be the images of these hexagons in A'. If h_1 and h_2 are in the same C-interior region then clearly their images in A' do not overlap, since translating the region does not change their positions relative to one another. Thus assume h_1 and h_2 are in different C-interior regions. If either hexagon is on the inside of the C-interior region to which it belongs, then the images of the two hexagons cannot overlap due to trivial distance considerations. (Any C-interior region is translated by a distance of at most s.) So assume both
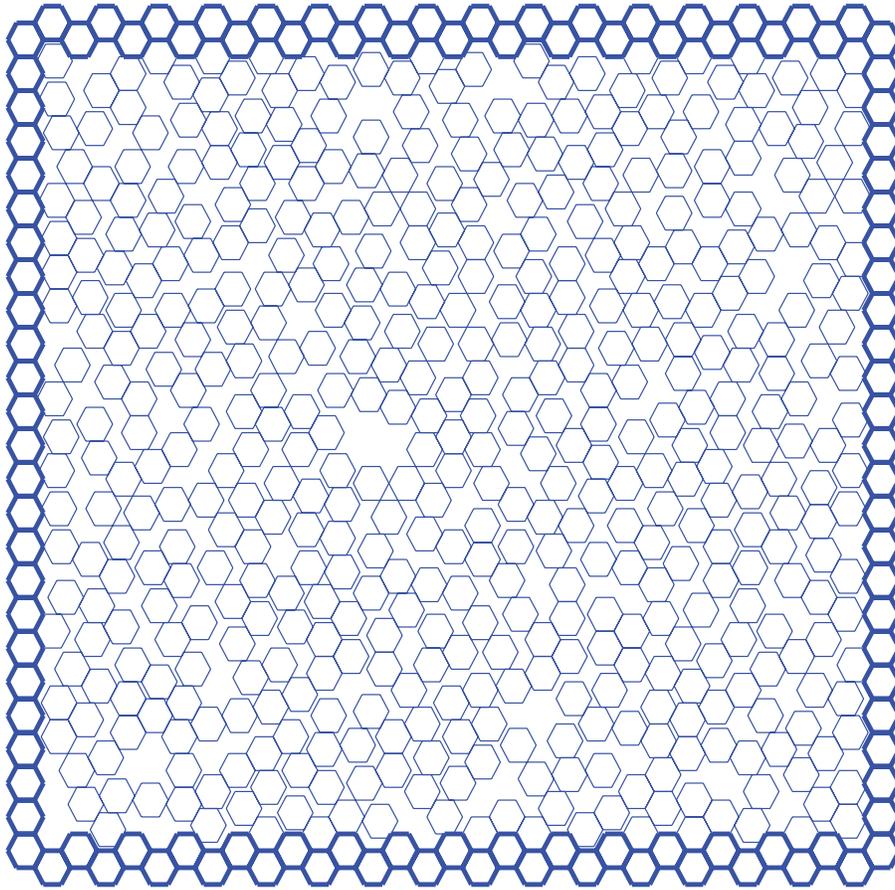
FIG. 5. (Color online) A plot of a configuration in equilibrium at $\mu = 1$.

hexagons are on the outside of distinct C-interior regions and write y_1 and y_2 for the centers of h_1 and h_2, respectively. Then $y_1 \in N_{x_1}$ and $y_2 \in N_{x_2}$ for some $x_1 \neq x_2$, since centers of distinct nonoverlapping hexagons must be in distinct neighborhoods. By definition of the map $A \to A'$, the hexagons h_1' and h_2' are centered at x_1 and x_2, respectively. Since x_1 and x_2 are distinct points in the boundary sublattice, h_1' and h_2' do not overlap, as desired.

Now, consider the image H' in A' of the set H of hexagons on the outsides of the C-interior regions of A. By definition of the map $A \to A'$, the hexagons in H' are on the boundary sublattice. Notice also that all the hexagons in H' remain in the region enclosed by C. Since C is an outer contour, the hexagons on the outer border of C are also on the boundary sublattice, and these hexagons are fixed by the map $A \to A'$. It follows that there is a void C' in A', which can be thought of as the "image" of C, such that C' is bordered by hexagons which are all on the boundary sublattice. The void C' can be therefore be covered by k nonoverlapping hexagons.

Let A'' be the image of A' under the map which fills C' with k nonoverlapping hexagons and fixes the rest of A'. We claim that $A'' \in \mathcal{T}$. All that must be shown is that each hexagon in A'' intersects one of the three upper edges of another hexagon. If h'' is the image of a hexagon on the inside of a C-interior region in A, then clearly this property holds true, since the relative local structures on the inside of C-interior regions do not change in the map $A \to A' \to A''$. On the other hand, if h'' is the image of a hexagon in the outside of a C-interior region, or if it is inside C', then this property also holds because C' is completely covered by nonoverlapping hexagons in A''.

Next we show that the correspondence $\mathcal{S} \to \mathcal{T}$ defined by $\mathcal{A} \to \mathcal{A}''$ is $1 - 1$. Suppose A_0 and A_1 are distinct configurations in $\mathcal{S}$. There is an obvious pairwise correspondence between the C-interior regions of A_0 and A_1. The outsides of corresponding C-interior regions of A_0 and A_1 are
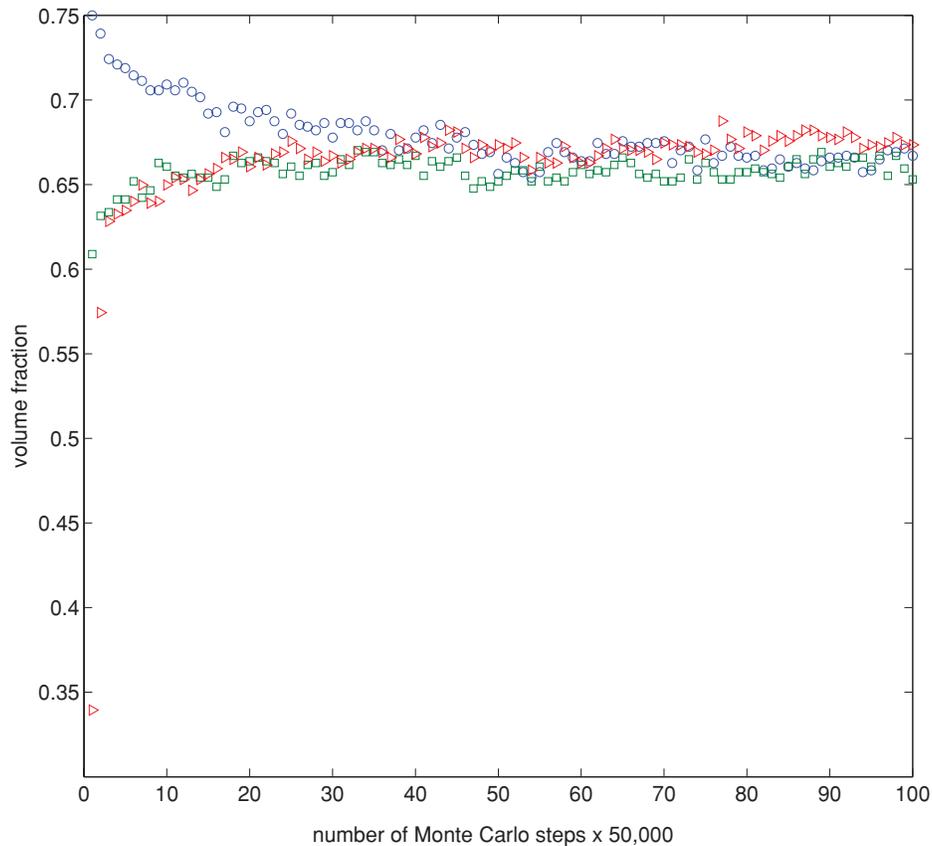
FIG. 6. (Color online) Plot of volume fraction versus number of moves, from three different initial volume fractions, for a system of volume 729 and $\mu = 1$.

identical because the contour defines these outsides. So since A_0 and A_1 are distinct, either at least one of these pairs of corresponding C-interior regions, say R_0 and R_1, have distinct insides, or A_0 and A_1 must be different outside the region enclosed by C. In the latter case A_0'' and A_1'' must be distinct because the map $A \rightarrow A''$ fixes everything outside the region enclosed by C. In the former case, the images of R_0 and R_1 are distinct and so A_0'' and A_1'' must also be distinct.

Using the correspondence $\mathcal{S} \rightarrow \mathcal{T}$ we can now put an exponential bound on the probability of seeing the outer contour C. Let $Z = Z_V$ be the normalization defined above, let H_n be the number of configurations A with the contour C and n hexagons, and let H_n'' be the number of configurations A'' with $n + k$ hexagons. By the above correspondence we have that $H_n'' \geq H_n$, and of course we also have that $\sum_{n=0}^{\infty} e^{(n+k)\mu} H_n'' \leq Z$. Thus, the probability of seeing the contour C is

$$\frac{1}{Z} \sum_{n=0}^{\infty} e^{n\mu} H_n \leq \frac{\sum_{n=0}^{\infty} e^{n\mu} H_n}{\sum_{n=0}^{\infty} e^{(n+k)\mu} H_n''} \leq e^{-k\mu}, \tag{1}$$

as desired.

Lemma 2: The number of contours C of size k (in units of hexagon area) enclosing the origin is less than $a_k b^k$, where $a_k = O(k^2)$ and b is constant. (Both a_k and b depend on s.)

Proof: Let C be a contour of area k (in units of hexagon area), such that C encloses the origin. Consider a graph with vertex set $L \cap C$ (recall that L represents the underlying triangular lattice). Join two vertices in the graph with an edge if they are nearest neighbors in L. Note that each connected component of this graph is at a distance of less than s from another component; join all the components by edges of length less than s.
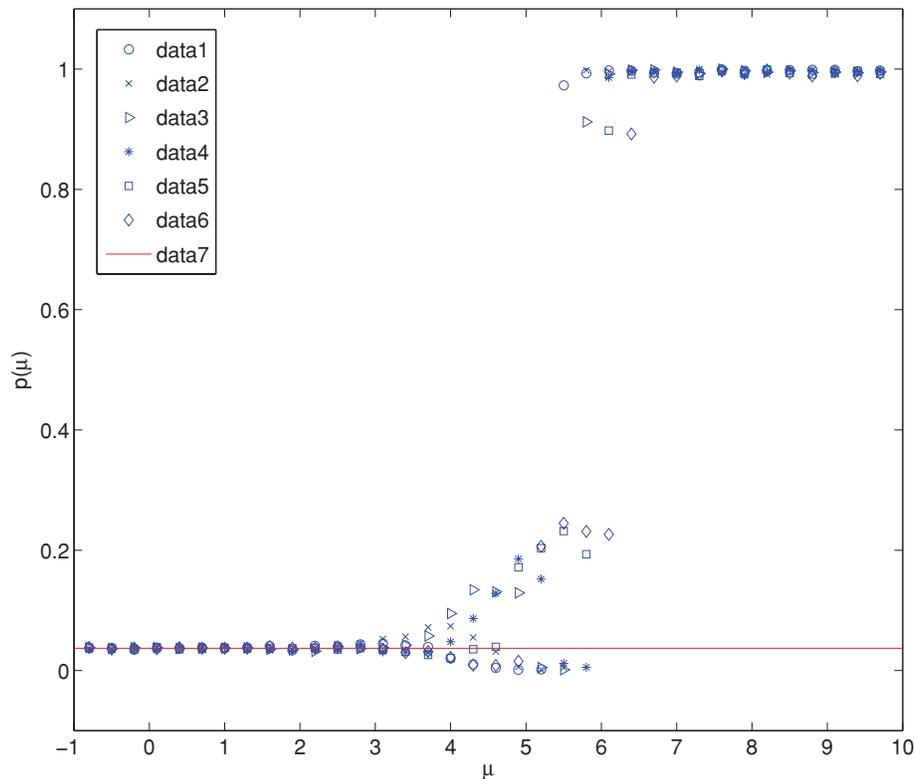
FIG. 7. (Color online) Plot of $p(\mu)$ vs μ for systems of volume 276 (data1) to 1151 (data6), for $s = 3$. Data7 is the line $p(\mu) = \frac{1}{3s^2} = \frac{1}{27}$.

Now we have a connected graph such that all its edges have length less than s. Consider a spanning tree for this graph, duplicate all the edges of the tree to get a graph G, and then choose a (directed) Eulerian path γ in G, that is, a path which traverses each edge in G exactly once. (It is a well-known fact of graph theory that Eulerian paths exists for such duplicate graphs.) Such a path covers all the points in $L \cap C$, so to upper-bound the number of possible contours C it suffices to upper-bound the number of such paths γ.

Since each hexagon contains $O(s^2)$ lattice points, the number of possible starting points for γ is $O(s^4 k^2)$. Also, since all the edges of γ have length less than s, given a point on γ there are $O(s^2)$ possibilities for the next point on γ. Observing that γ traverses $O(s^2 k)$ points, the result follows.

Proof of Theorem 1. From Lemmas 1 and 2, we find that the probability of seeing an outer contour enclosing the origin is no greater than $\sum_{k>0} a_k (\exp(-\mu)b)^k$, and this sum can be made arbitrarily small for μ sufficiently large. Recall that if there is no hexagon centered at the origin, then there is an outer contour enclosing the origin. Since the latter event has arbitrarily small probability for μ sufficiently large, the former must also; one concludes, therefore, that the probability there is a hexagon centered at the origin is arbitrarily large for μ sufficiently large. This probability is smaller than the conditional probability $p(\mu)$, so we conclude that $p(\mu) > (3s^2)^{-1}$ for μ sufficiently large, as desired.

We wish to emphasize that the result of Theorem 1 holds for any fixed finite hexagon side length s; it does not hold true in the "continuum" limit $s \to \infty$.

IV. LOW DENSITY

As noted in the introduction, granular systems do not exist at very low density, and we cannot hope to understand low density behavior as a perturbation of a state of independent particles. We
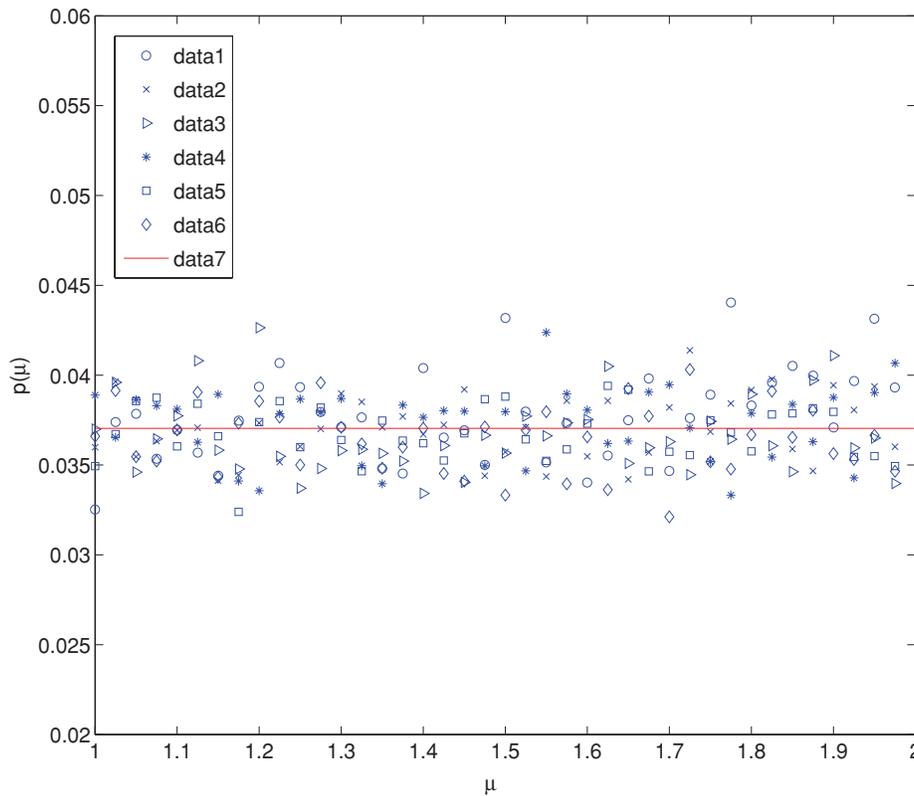
FIG. 8. (Color online) Plot of $p(\mu)$ vs μ for systems of volume 276 (data1) to 1151 (data6), for $s = 3$. Data7 is the line $p(\mu) = \frac{1}{3s^2} = \frac{1}{27}$.

expect that granular matter and our model are disordered at low density but we could not prove this. Instead, we ran Markov chain Monte Carlo simulations on the model for a range of values of μ. As is typical of simple simulations such as ours, the confidence intervals one obtains would hold rigorously if only one could prove that our runs were long enough so that we were sampling the target probability distribution.[6] This is rarely possible in practice, in which case one relies on standard guidelines such as mixing times for this purpose; see for instance Ref. 1.

Our goal in this section is to show that in the infinite volume limit the boundary has no influence near the origin for small positive μ. More precisely, we will argue that $p(\mu)$, the quantity defined in Sec. I, is constant and equal to $(3s^2)^{-1}$ in some interval of positive length above $\mu = 0$. Our argument will concentrate on the interval $[1, 2]$ for μ. (For much lower μ the configurations look like "seaweed," or disconnected vertical wavy columns, as in Fig. 4. We do not know how the model connects this seaweed regime from that of the highly connected configurations that one sees for $\mu > 0$. We have avoided this complication by only studying μ near the target transition; compare Figs. 4 and 5.)

We checked that our Monte Carlo runs were not sensitive to the initial condition (see Fig. 6); since initial conditions at lower volume fractions tended to equilibrate faster, we started most of our Monte Carlo runs with void configurations. To obtain numerical estimates of $p_V(\mu)$ we considered the following functions of our Monte Carlo configurations. For a configuration A we let $\delta(A) = 1$ if there is a hexagon in A centered at the origin; we let $\delta(A) = 0$ otherwise. We define $t(A) = 1$ if there is a hexagon in A centered at a point in the neighborhood N_O of the origin, and $t(A) = 0$ otherwise.

For systems ranging in volume from 276 to 1151 (in units of hexagon volume) we evaluated δ and t on configurations $A_1, A_2, \ldots$, and for each system size V we consider the following statistic:

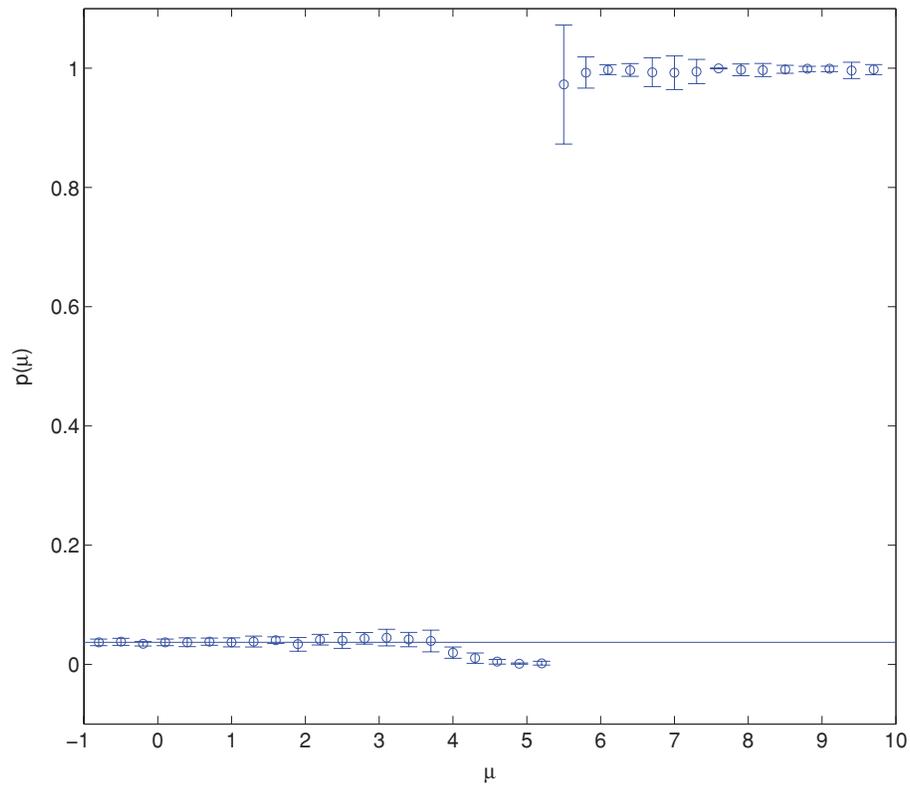$$p_M := \frac{\delta(A_1) + \delta(A_2) + \cdots + \delta(A_M)}{t(A_1) + t(A_2) + \cdots + t(A_M)}. \tag{2}$$

FIG. 9. (Color online) Plot of $p(\mu)$ vs μ for a system of volume 276, with error bars, for $s = 3$. The line is $p(\mu) = \frac{1}{3s^2} = \frac{1}{27}$.
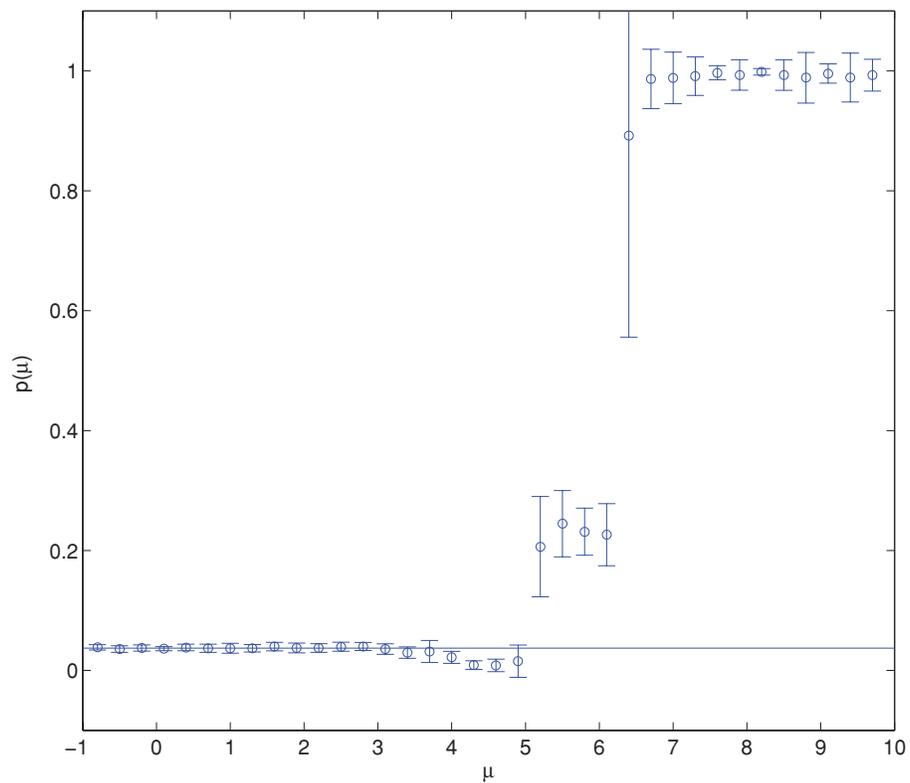

FIG. 10. (Color online) Plot of $p(\mu)$ vs μ for a system of volume 1151, with error bars, for $s = 3$. The line is $p(\mu) = \frac{1}{3s^2} = \frac{1}{27}$.
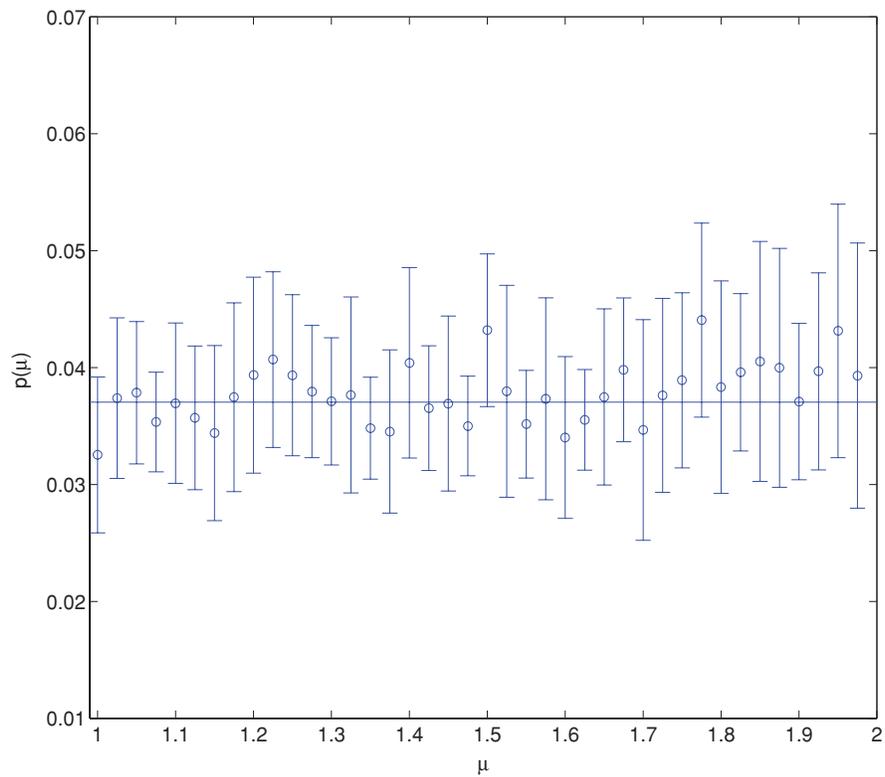
FIG. 11. (Color online) Plot of $p(\mu)$ vs μ for a system of volume 276, with error bars, for $s = 3$. The line is $p(\mu) = \frac{1}{3s^2} = \frac{1}{27}$.
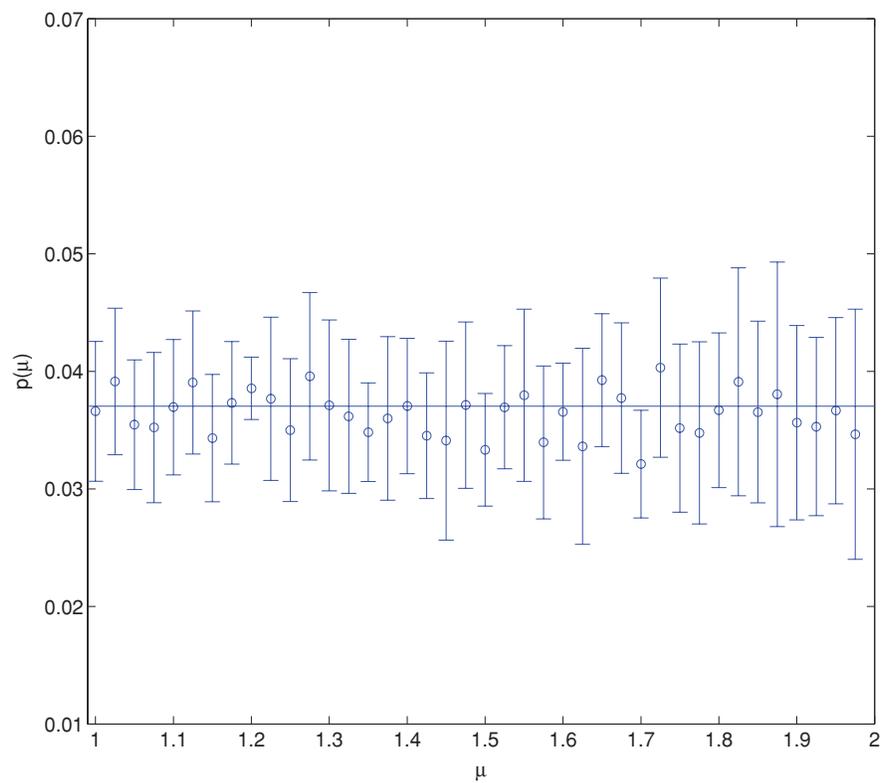

FIG. 12. (Color online) Plot of $p(\mu)$ vs μ for a system of volume 1151, with error bars, for $s = 3$. The line is $p(\mu) = \frac{1}{3s^2} = \frac{1}{27}$.
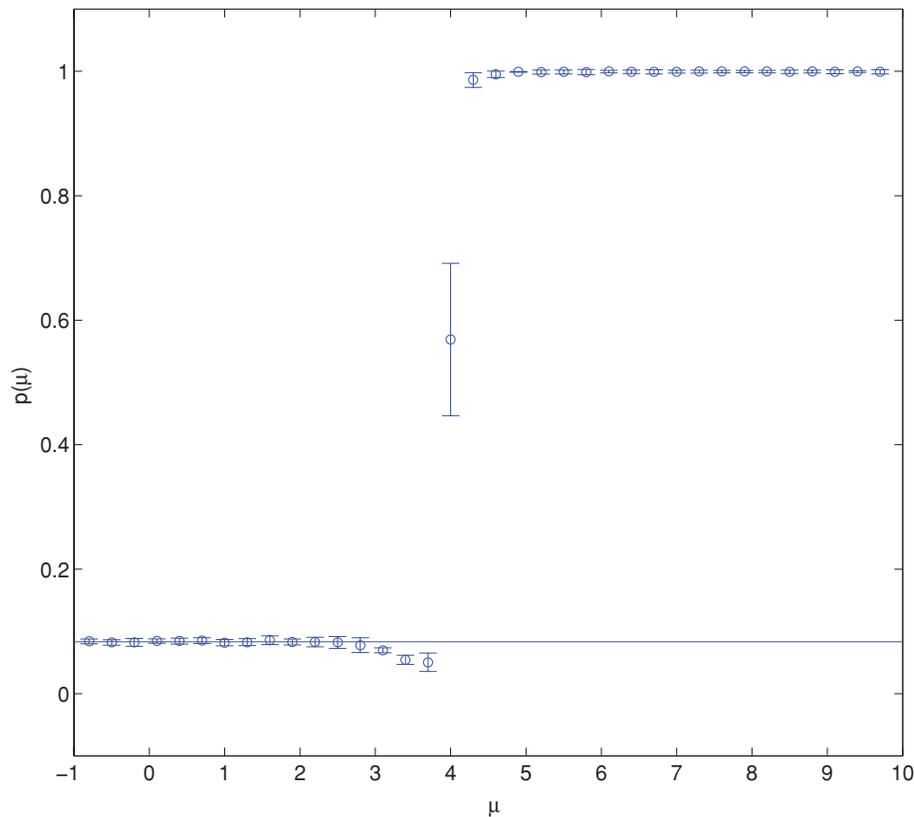
FIG. 13. (Color online) Plot of $p(\mu)$ vs μ for a system of volume 276, for $s = 2$. The line is $p(\mu) = \frac{1}{3s^2} = \frac{1}{12}$.

So the expected value of p_M is exactly $p_V(\mu)$. We obtain 95% confidence intervals for p_M in the same way as in Ref. 1; in particular we determine the mixing time for our simulations using the biased autocorrelation function on volume fraction data, and then use the common method of batch means[6] with about 10 batches for each run. The batch size M is chosen so that there are at least 5 mixing times per batch, except in the transition region. (Our 95% confidence intervals would be rigorous if we could prove we were truly sampling from the target distribution; the mixing time criterion is a nonrigorous way to argue that we are very close to doing just that.[6])

If the boundary has no influence near the origin, hexagons should be centered on each of the $3s^2$ sublattices with equal probability, so we expect that $p(\mu)$ is exactly $(3s^2)^{-1}$ for small μ. In Figs. 7–12 we compare data from our Monte Carlo runs to the line $y = (3s^2)^{-1}$, with $s = 3$. For $\mu \in [0, 4]$ the data suggest that $p_V(\mu)$ follows the line; then in the range $\mu \in [4, 6]$, $p_V(\mu)$ increases to about 1; for $\mu > 6$, $p_V(\mu)$ stays near the line $y = 1$. In Figs. 11 and 12 we consider more detailed data for μ in [1, 2]. Our 95% confidence intervals cover the line $y = (3s^2)^{-1}$ more than 95% of the time, as appropriate. We conclude that our simulated values of $p_V(\mu)$ inside the interval [1, 2] and inside the interval [0, 10] suggest that $p(\mu)$, which is the limit of $p_V(\mu)$ as $|V| \to \infty$, is indeed constant for small positive μ and, in particular, is constant inside [1, 2] (see Figs. 7–14).

It is important to note that $p_V(\mu)$ is analytic for any finite V, so one cannot hope for $p_V(\mu)$ to be identically equal to $(3s^2)^{-1}$ at low μ. For all of our systems, however, we find $p_V(\mu)$ to be within (small) error bars of $(3s^2)^{-1}$ for $\mu \in [1, 2]$, so we find it reasonable to expect that $p(\mu)$ is identically $(3s^2)^{-1}$ for $\mu \in [1, 2]$. (To use simulation to show that *dependence* on the boundary survives in the infinite volume limit requires careful study of the size of the simulation samples, while the burden is easier to show *independence* of the boundary, as we do.)

We note that the transition region changes as s increases. In particular, as s increases the smallest value of μ such that $p(\mu) > (3s^2)^{-1}$ seems also to increase; compare Figs. 9, 13, and 14.
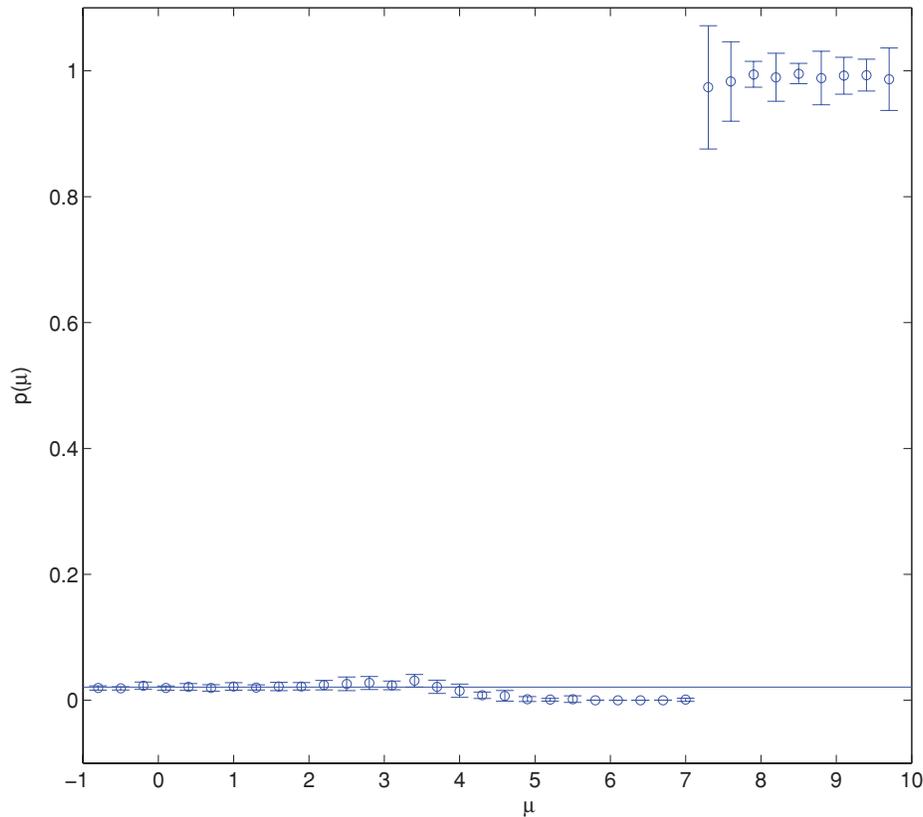
FIG. 14. (Color online) Plot of $p(\mu)$ vs μ for a system of volume 276, for $s = 4$. The line is $p(\mu) = \frac{1}{3s^2} = \frac{1}{48}$.

V. CONCLUSION

We find a phase transition in a toy model which is a granular variant of equilibrium lattice hard hexagon models. The transition is associated with the granular phenomenon of random close packing. It is signalled in our model by the order parameter $p(\mu)$, the probability that a hexagon near the origin is on the same sublattice as the boundary hexagons. (Recall μ is a parameter controlling volume fraction.) We have proven that for sufficiently large positive μ, $p(\mu)$ is greater than $(3s^2)^{-1}$ (where $3s^2$ is the number of distinct sublattices), and in fact $p(\mu)$ approaches 1 as $\mu \to \infty$. In addition we have numerical evidence that in an interval above $\mu = 0$, $p(\mu)$ has the constant value $(3s^2)^{-1}$, which is indicative of disorder. As the two types of behavior of $p(\mu)$ cannot be connected analytically we conclude[5] that the model undergoes a phase transition at some positive μ. The transition can be seen in Fig. 9, but it would take much more simulation to demonstrate singular behavior at a specific value of μ. Instead, our argument for the existence of a transition is based on failure of analyticity of $p(\mu)$.

The transition we have found is of the order/disorder type since the long range order which we prove to hold at large μ is absent at low μ. This is consistent with our goal to understand random close packing: the sudden appearance of crystalline structure in granular matter at a given density. We note that, as usual in hard-core lattice models,[8] our results only apply for a finite ratio s of hexagon size to lattice spacing; our upper bound on ordered behavior diverges as $s \to \infty$.

In conclusion, we have shown that a granular adaptation of the hard hexagon model has an order/disorder phase transition by combining a proof of ordered behavior at high density with Monte Carlo evidence showing disordered behavior at low density. This approach is necessarily distinct from that of models in equilibrium statistical mechanics, because for the latter it is trivial to show disordered behavior at low density since particles are nearly independent. One lesson from this work is the need for a new technique in understanding disordered phases in statistical physics. More

generally, familiar technical results concerning the infinite volume limit for equilibrium statistical mechanics will need to be adapted to the granular setting (see, for instance, Ref. 2).

ACKNOWLEDGMENT

[1] Aristoff, D. and Radin, C., "Random loose packing in granular matter," J. Stat. Phys. **135**, 1 (2009).

[2] Aristoff, D. and Radin, C., "Dilatancy transition in a granular model," e-print arXiv:1005.1907.

[3] de Gennes, P. G., "Granular matter: A tentative view, " Rev. Mod. Phys. **71**, S374 (1999).

[4] Edwards, S. F. and Oakeshott, R. B. S., "Theory of powders," Physica A **157**, 1080 (1989).

[5] Fisher, M. E. and   Radin, C., Definitions of thermodynamic phases and phase transitions, workshop report, http://www.aimath.org/WWN/phasetransition/Defs16.pdf.

[6] Geyer, C. J., "Practical Markov chain Monte Carlo," Stat. Sci. **7**, 473 (1992).

[7] Ginibre, J., "On some recent work of Dobrushin," in *Systèmes à un nombre infini de degrés de liberté* (CNRS, Paris, 1969), pp. 163–175.

[8] Heilmann, O. J. and Prastgaard, E., "Phase transition of hard hexagons on a triangular lattice," J. Stat. Phys. **9**, 23 (1973).

[9] Lee, T. D. and Yang, C. N., "Statistical theory of equations of state and phase transitions. II. Lattice gas and Ising model," Phys. Rev. **87**, 410 (1952).

[10] Monasson, R. and Pouliquen, O., "Entropy of particle packings: An illustration on a toy model," Physica A **236**, 395 (1997).

[11] Nicolas, M., Duru, P., and Pouliquen, O., "Compaction of a granular material under cyclic shear," Eur. Phys. J. E **3**, 309 (2000).

[12] Radin, C., "Random close packing of granular matter," J. Stat. Phys. **131**, 567 (2008).

[13] Ruelle, D., *Statistical Mechanics; Rigorous Results* (Benjamin, New York, 1969).

[14] Scott, G. D., Charlesworth, A. M., and Mak, M. K., "On the random packing of spheres," J. Chem. Phys. **40**, 611 (1964).