

## Some Observations on the Random Packing of Hard Ellipsoids

P. M. Chaikin,<sup>\*,†,‡</sup> Aleksandar Donev,<sup>‡,§</sup> Weining Man,<sup>||,⊥</sup> Frank H. Stillinger,<sup>#</sup> and Salvatore Torquato<sup>‡,§,¶,∇</sup>

*Department of Physics and Center for Soft Condensed Matter Research, New York University, New York, New York 10003; Princeton Institute for the Science and Technology of Materials, Princeton University, Princeton, New Jersey 08544; Program in Applied and Computational Mathematics, Princeton University, Princeton, New Jersey 08544; Department of Physics, Princeton University, Princeton, New Jersey 08544; Department of Chemical Engineering, Princeton University, Princeton, New Jersey 08544; Department of Chemistry, Princeton University, Princeton, New Jersey 08544; Princeton Center for Theoretical Physics, Princeton University, Princeton, New Jersey 08544*

Recent studies of random packing of ellipsoids show a cusplike increase in the packing density as the aspect ratio deviates from 1 (spheres) followed by a maximum and then a strong density decrease at a higher aspect ratio. We introduce a simple one-dimensional model, the “Paris” parking problem with ellipses randomly oriented along a curb, with many of the same features. Our results suggest that the cusp results from approaching a terminal (jammed) random state, the density increase results from relaxing a parameter constraint (orientation or size of a particle) in the random packing, and the density decrease results from excluded volume effects. We also discuss the isostatic conjecture for strict and local jamming.

### Introduction

The work of our colloid group, a collaboration with Professor Bill Russel, has centered on hard spheres and their phase transitions and dynamics. The present study of hard particle packing problems is an outgrowth of that collaboration. Indeed, Professor Russel had significant input to these studies, providing several of the basic ideas as well as insights into experimental approaches and analysis. The work on ellipsoids is directly related to the colloid group’s studies of hard sphere glasses<sup>1</sup> and the effects of polydispersity<sup>2</sup> on packing and on frustrating crystallization.

As we discuss below, the formation of crystals from simple liquids is often entropically driven by the different packing densities of disordered and ordered spheres.<sup>3–7</sup> In moving to more complex shapes, with an eye toward forming new phases and toward using colloids to build interesting and active structures, the natural first step was to try the simplest deformation of a sphere. An ellipsoid is obtained from a sphere by an affine deformation, a linear change such as rescaling a coordinate axis. An interesting question was how this simple deformation could change the packing properties. The original experiments on m&m candies<sup>8,9</sup> found higher random packing densities<sup>10</sup> and higher mean contact number than for spheres.<sup>11</sup> This led to a numerical study of the packing fraction,<sup>12</sup>  $\phi_c$ , and mean contact number,  $Z$ , as a function of aspect ratio,  $\alpha = a/b$ , for the maximally random jammed (MRJ) state,<sup>10</sup> as shown in Figures 1 and 2. Roughly speaking, the MRJ state can be thought of as the “most random” (that is, the least ordered in terms of

a number of order metrics) state, subject to the constraint that the packing is “jammed.” The results were quite dramatic in that both  $\phi_c$  and  $Z$  were singular functions of  $\alpha$  at the sphere point with a downward cusp and a linear increase in  $\phi_c$  for small  $\alpha$ . Moreover, the mean contact number tended to saturate at near the conjectured isostatic point<sup>13,14</sup> for large  $\alpha$ , while the packing fraction decreased.

The experiments and simulations raised many fundamental questions, some of which we address here. The isostatic conjecture suggests that, for stability, the mean contact number should be equal to twice the number of degrees of freedom ( $f$ ),  $Z = 2f$ . If this were true, then we should see a discontinuous jump in  $Z$  on leaving spherical symmetry. We here reexamine the isostatic conjecture and present ways around it. The shape of the packing fraction vs  $\alpha$  needs understanding, and we present here a simple system, a 1D parking problem with ellipses which has many of the same features. This leads us to suggest that the density increase is due to additional degrees of freedom, the cusp is due to the singular nature of a random jammed state (for definitions of the hierarchy of jammed states such as local, collective, and strict, see refs 15 and 16), and the decrease at high  $\alpha$  is an excluded volume effect. The latter was originally seen in spherocylinders by Williams and Philipse.<sup>17</sup> We make some comparisons between ellipsoids and spherocylinders below. Finally we present some data on the packing density of pennies in a jar.

### Thermodynamics of Hard Particles

The packing problem has a great deal of relevance to physics and, in particular, to the existence of the crystalline state and the nature of the melting transition. For hard particles, the potential energy is zero when particles do not overlap and infinite when they interpenetrate. They, therefore, never touch, and the potential energy is identically zero. The state with the highest entropy is the stable state. The easiest example of an entropic system is an ideal gas where  $S = k_B \ln V$ . van der Waals noted that one of the first corrections to ideal gas behavior is to account for the fact that particles occupy a certain volume which is excluded from occupation by the other particles. For hard particles in one dimension, this can be treated exactly by

\* To whom correspondence should be addressed. Tel.: (212) 998-7694. E-mail: chaikin@nyu.edu.

<sup>†</sup> Department of Physics and Center for Soft Condensed Matter Research, New York University.

<sup>‡</sup> Princeton Institute for the Science and Technology of Materials, Princeton University.

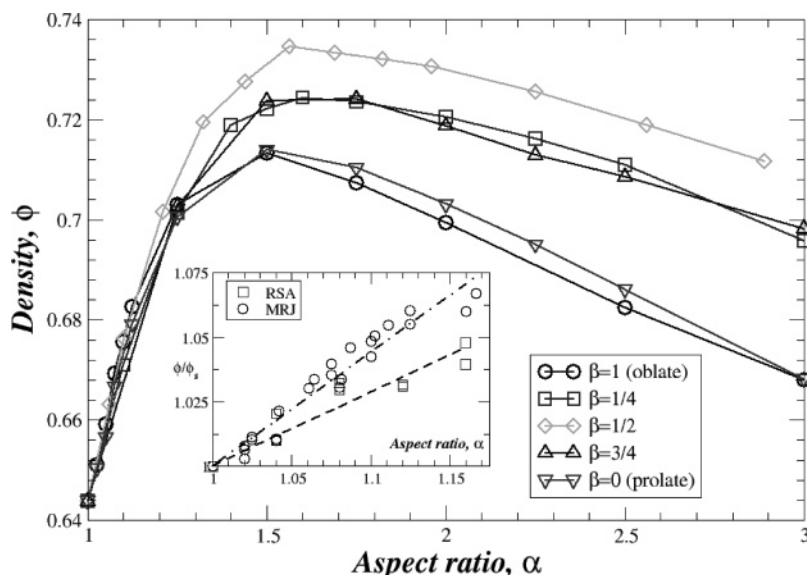
<sup>§</sup> Program in Applied and Computational Mathematics, Princeton University.

<sup>||</sup> Department of Physics, Princeton University.

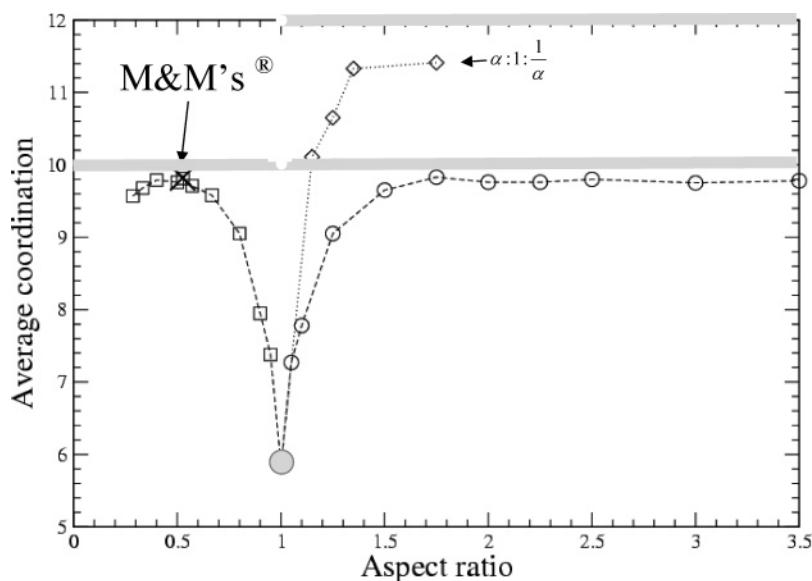
<sup>⊥</sup> Department of Chemical Engineering, Princeton University.

<sup>#</sup> Department of Chemistry, Princeton University.

<sup>∇</sup> Princeton Center for Theoretical Physics, Princeton University.



**Figure 1.** Packing fraction vs aspect ratio for 10 000 particles. The semiaxes are  $1/\alpha^\beta/\alpha$ . Inset shows linear dependence for both MRJ<sup>10</sup> ( $10^3$ – $10^4$  particles) and RSA ( $10^3$  particles) simulations



**Figure 2.** Mean contact number as a function of aspect ratio for MRJ.<sup>10</sup> Light gray point and lines are expected behavior from the “isostatic conjecture”.

simply subtracting the length of the particles from the total length of the box they are in.  $V \rightarrow V - Nb$ , where  $N$  is the number of particles of volume (length)  $b$ . Factoring out  $V$ , we have  $V(1 - \phi/\phi_c)$  and  $S = k_B \ln[V(1 - \phi/\phi_c)]$ , where  $\phi$  is the volume fraction and  $\phi_c$  is the highest volume fraction for the particular configuration, i.e., the jamming density. In one dimension,  $\phi_c = 1$ . The pressure is related to the volume derivative of  $S$ ,  $P = nk_B T / (1 - \phi/\phi_c)$  and diverges at close packing. Although the above expressions for  $S$  and  $P$  are exact only in one dimension, the form is exact in any dimension for infinitesimal deviations from a jammed configuration.<sup>16,22</sup> In particular,

$$S \rightarrow Nk_B \ln(V(1 - \phi/\phi_c))|_{\phi \rightarrow \phi_c} \quad P \rightarrow \frac{dnk_B T}{(1 - \phi/\phi_c)}|_{\phi \rightarrow \phi_c}$$

For the case of hard spheres where  $\phi_c \approx 0.64$  for MRJ packing and  $\phi_c \approx 0.74$  for FCC packing, this implies that, as  $\phi \rightarrow 0.64$ , the entropy of the crystal state is higher than that of the liquid state. (We note that, more generally, the spatial

dimension  $d$  in the pressure equation should be replaced by  $f$ , the number of degrees of freedom of the particle.) Thus, before reaching  $\phi = 0.64$ , there must be an entropy-driven transition to the crystal. These arguments form the basis of many theories of the melting of simple liquids.<sup>18</sup>

The reason these arguments are of interest in our present work is the conclusion that, at high density, it is always the densest packed phase that is thermodynamically stable. If a particular shape of ellipsoids were to pack better randomly than in a crystalline array, then it would not crystallize. As the density increased, the system would remain amorphous and might form an ideal glass. So far, we have not found any system in which random packing is denser than a crystal packing, but there are still many simple systems, e.g., ellipsoids<sup>21</sup> and tetrahedra, where the densest packings are not known. There are interesting suggestions that, in higher dimensions, even sphere packings may be denser in a random configuration than in an ordered configuration.<sup>19</sup> We also note that the driving force to crystallization is the entropy difference between the disordered and ordered phases, and this is related to the different packing

fractions. For spheres, the large difference in  $\phi_c$ , 0.64 vs 0.74, makes crystallization easy to observe both in colloidal systems and in computer simulations. The smaller difference between  $\phi_c$  for some random<sup>9</sup> vs crystalline ellipsoids,  $\phi_c \approx 0.74$  vs 0.747,<sup>21</sup> reduces the thermodynamic drive for freezing, while the additional rotational degrees of freedom may make the formation of nuclei more difficult. Indeed, simulations have not yet found crystallization for ellipsoids with  $\alpha > 1.2$ , although several groups have tried.<sup>20</sup>

### Spherocylinders

There has been some beautiful work on the random packing of spherocylinders<sup>17</sup> which slightly predates our studies of ellipsoids. Both systems are interesting and show similar curves of packing fraction vs aspect ratio. There is an initial increase in packing density, while at large aspect ratios, the density decreases dramatically. The work by Williams and Philipse is largely concerned with the decrease in  $\phi_c$  for long cylinders and suggests that this is an excluded volume effect. We tend to agree with that interpretation, which is consistent with our results from the Paris parking problem described below. However, it is not as clear that the behavior at low aspect ratios arises from the same effects for ellipsoids as for spherocylinders. Ellipsoids are an affine deformation of spheres, and therefore, we have several exact results to fall back on in interpreting our findings. Two of the most surprising results for the random packing of ellipsoids are the increase of the packing fraction as one moves away from the sphere,  $\alpha = 1$ , and the observation that the sphere is a singular point on the curve. For ellipsoids, the shape is a continuous function of the aspect ratio, while for spherocylinders, a sphere is already a singular point. One way of seeing this difference is to see how the deformations affect the densest crystal packing. If we start at the FCC lattice, then an affine deformation changes the volume of each particle and the volume of the confining space the same way. The lattice packing remains unchanged at 0.74. (Even if we use the densest ellipsoid packing yet discovered,<sup>21</sup> the packing fraction increases in a quadratic manner from  $\alpha = 1$ .) On the other hand, the (probable) densest packing of spherocylinders is obtained by adding a cylindrical region on the planes of the sphere centers of the FCC lattice. The packing fraction then gives a plane spacing weighted average between the FCC and the infinite cylinder packing

$$\phi = (\phi_{\text{FCC}}\sqrt{2/3}d + \phi_{\text{CYL}}l)/(\sqrt{2/3}d + l) \approx \phi_{\text{FCC}} + ((\alpha - 1)/d)\sqrt{3/2}(\phi_{\text{CYL}} - \phi_{\text{FCC}})$$

where  $d$  is the diameter,  $l$  is the added length of the cylinder,  $\alpha = (d + l)/d$ ,  $\phi_{\text{FCC}} = \pi/\sqrt{18}$ ,  $\phi_{\text{CYL}} = \pi/\sqrt{12}$ , and the approximation is for small  $\alpha - 1$ . For spherocylinders, the crystal packing fraction increases linearly in  $\alpha - 1$  with a slope that is comparable to the increase in random packing fraction.

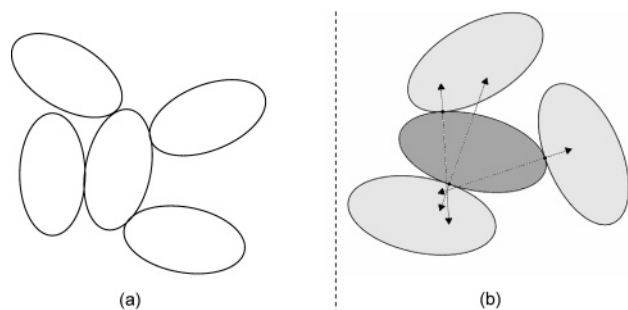
Thus, although there is a linear increase in the random packing density for spherocylinders (hence, a “cusp”), it is not clear whether this is due to the singular shape change or the additional rotational degrees of freedom. Moreover, for spherocylinders, the random packing fraction does not approach the crystal packing as aspect ratio is increased. The similarity between ellipsoid and spherocylinder packing does reemerge at large aspect ratios, where both are dominated by the excluded volume effects that greatly decrease the packing fraction.

### Isostatic Conjecture

In its most common usage, the isostatic conjecture states that, for a mechanically stable large random packing of hard

frictionless particles, the mean contact number or number of touching neighbors per particle is just twice the number of degrees of freedom per particle.<sup>13,14</sup> There are two assumptions: (1) to fix the positions and orientations, at least as many constraints as degrees of freedom are needed and (2) disordered packings will have the minimal number of contacts necessary, since forming additional contacts introduces additional correlations. For hard (frictionless) particles, the constraints come from contacts with each contact involving two neighbors, hence, one contact and two neighbors per particle per degree of freedom on average. Part of our intuition as to why ellipsoids pack more densely than spheres comes from the idea that, for shapes close to spherical, if the number of degrees of freedom increases (for ellipsoids orientation is important) and the number of contacts must increase, then this should be associated with a density increase. In fact, for our early experiments on m&m's, the most interesting finding was confirmation of the isostatic conjecture. Randomly packed spheres with three degrees of freedom (translations in 3D) have close to 6 neighbors, and m&m's with five degrees of freedom have close to 10 neighbors.<sup>11</sup>

Simulations of ellipsoid packing also indicate that the number of neighbors for ellipsoids of revolution, spheroids (five degrees of freedom), approaches 10 neighbors, and for ellipsoids with three different axes and six degrees of freedom, it approaches 12 neighbors. However, the isostatic conjecture would suggest that an infinitesimal deviation from sphericity would require a jump from 6 to 12 contacts, and this is both difficult to reconcile physically and not supported by simulations. Thus, either the conjecture is not applicable universally or our understanding of the simulations and/or the concept of jamming for ellipsoids is incomplete. One problem in applying the isostatic conjecture to ellipsoids is that the precise meaning of jammed (or rigid) is unclear, especially close to the sphere point. (Note that, in ref 9, an affine transformation of the densest crystal packing of spheres, which is strictly jammed, leads to a crystal packing of ellipsoids that can be sheared and, therefore, is not strictly jammed.) We can define jamming similarly to the way we do for spheres, but it is not clear that this is really appropriate. Moreover, we cannot test for jamming in ellipsoid packings as we can for spheres.<sup>22</sup> Therefore, we cannot rigorously prove that the simulated ellipsoid packings near the sphere point are truly jammed. So we revisit the ideas and assumptions in a slightly different treatment than in the published literature. The basic idea is that, for the system to be at stable equilibrium for each particle, the sum of the forces and the sum of the torques must be zero.<sup>23</sup> In the absence of body forces (e.g., gravity), the only forces are from the contacts,  $\sum_{\text{Contacts}} F_i = 0$ , and there are  $d$  force equations from the  $d$  spatial dimensions. Torques arise from forces at the contacts:  $\sum_{\text{Contacts}} (\mathbf{r} \times F)_i = 0$ , where  $\mathbf{r}$  is the vector from the center of mass (for each particle) to the contact point. The maximum number of torque equations,  $n$ , is  $n_{\text{max}} = d(d - 1)/2$  ( $n = 1$  in 2D, 3 in 3D). The conjugate displacements are the degrees of freedom,  $f$ . Thus  $f = d + n$ , and the total number of equations is  $fN$  for  $N$  particles. The unknowns in the problem are the  $F_i$ 's at the contacts, which number  $dN_c$  for  $N_c$  total contacts. Since each contact is shared between two particles, the average mean contact number is  $Z = 2N_c/N$ . In order for the linear system of equations describing the force/torque equilibrium to have a unique nontrivial solution that is also stable against slight perturbations (of the geometry, or the application of small random loads on each particle, as in shaking the packing), the number of equations equals the number of unknowns,  $dN_c = fN$ ,  $N_c/N = f/d$ ,  $Z = 2fd$ . This is the case for *frictional* particles where both tangential forces and rotations



**Figure 3.** Local jamming (outer particles are held fixed): (a) usually four contacts constrain an ellipse, but (b) three contacts whose normals intersect also work.

are relevant (even for spheres),  $f = d + d(d - 1)/2 = d(d + 1)/2$ ,  $Z = d + 1$ . It is also possible that a torsional force normal to the surface may be applied which resists twisting the object under the contact point. This torsional force complicates the torque equations but does not change their number. It does increase the number of unknowns at each contact from  $d$  to  $d + 1$ . We then have  $(d + 1)N_c = fN = Nd(d + 1)/2$ ,  $N_c/N = d/2$ ,  $Z = d$ . In 3D,  $Z = 3$ . The torsional force is inapplicable in one and two dimensions.

On the other hand, for frictionless particles, the only component of the force that is relevant is the normal force, and there is an additional set of equations which requires tangential forces to be zero at each contact ( $n \times F_i = 0$ ). This amounts to  $(d - 1)N_c$  equations, and setting the number of unknowns (forces at each contact) equal to the number of equations gives  $dN_c = (d - 1)N_c + fN$  or  $N_c = fN$ ,  $N_c/N = f$ ,  $Z = 2f$ . This is the *frictionless* isostatic result. Note that, for spheres, the normal to the surface is also a radial vector, so that the frictionless constraint is equivalent to a torque equation. Since the sphere rotation then has no relevance, the rotations are not included in the degrees of freedom.

If the number of equations equals the number of unknowns, then a solution can be found for a configuration and perturbations lead to nearby solutions. If there are more equations than unknowns, there may be no solutions or there may be particular solutions which are not stable to perturbations and form a less dense set. For more unknowns than equations, there are multiple solutions. The conjecture in the isostatic conjecture is that a random jammed system is minimally constrained in the sense that the number of unknowns and equations is equal. Part of the reasoning is that neither the contacts nor the forces are correlated in a random system. The reasoning requires that degenerate geometries such as that of Figure 3 above do not occur frequently.

There can be cases in which the constraints can be satisfied by particular arrangements with fewer contacts. An illustrative example is seen in Figure 3, which shows a locally constrained ellipse. For local jamming of spheres, one requires  $(d + 1)$  contacts, with the extra 1 to prevent escape. In general, one imagines that four contact points are needed to fix the position and orientation of the center ellipse (Figure 3a). However, the three neighbors in Figure 3b also completely confine the central ellipse because they are arranged so that the normals from the points of contact meet at the same point and the curvature of the ellipse on at least one of the points of contact is sufficiently “flat” to prevent rotations of the ellipse. This example demonstrates that one can, in fact, have a jammed system with fewer constraints than the number of degrees of freedom and contradicts a statement by S. Alexander “One requires 4 (=3 + 1) contacts to fix the three DOF ... of an ellipse in the plane”

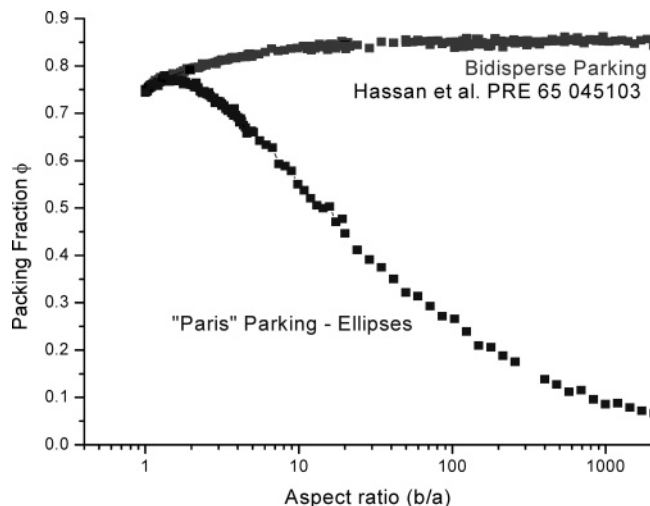
[cf. Section 15.5.1 in ref 24] if to “fix” and to “jam” have the same meaning.<sup>24</sup> The (infinite) number of ways that the three contact configurations can constrain the ellipse is a zero measure set compared to the number of ways with the four contacts. Nonetheless, when the three fixed ellipses are positioned such that the central ellipse cannot escape by translation and rotation, then as the ellipses are grown in size (e.g., in a Lubachevsky–Stillinger algorithm),<sup>25</sup> the central ellipse will always find the locally jammed configuration. This suggests that, in the three-dimensional ellipsoid problem, the jammed state may likewise find a more correlated configuration with many fewer arrangements, in some sense lower “entropy”, than would be expected for complete randomness or isostaticity. This reduction in effective phase space may be similar to the nonergodicity found in many glassy systems.

### Random Sequential Addition

Probably the simplest packing problem is the “parking problem” or random sequential addition, RSA,<sup>15</sup> in the infinite-time one-dimensional case. In the parking problem,<sup>26</sup> cars of equal length randomly pull up to a curb and park at the spot of their first try if there is sufficient room for their length between the other parked cars. Assuming the parking attempts are uncorrelated, the question is, what is the maximum coverage of the curb space for an infinitely long curb? RSA is the generalization of this process to impenetrable objects randomly placed sequentially in a  $d$ -dimensional space. The coverage increases with the number of attempts and finally saturates. The saturated state is a terminal state in which a particle can no longer be added to the packing. In this sense, the saturated state may be thought of as a “jammed” state, even though the average contact number is exactly zero.

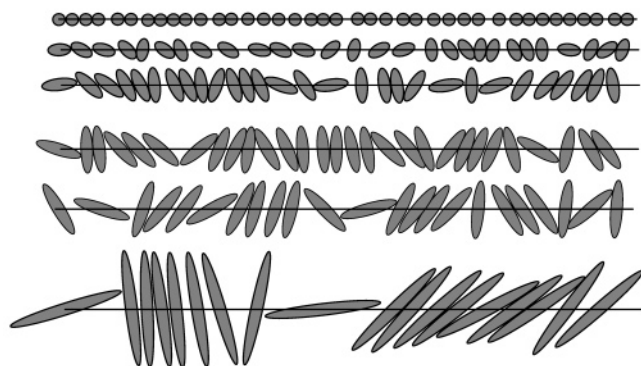
We would like to see whether we can learn something about the behavior of the random packing of ellipsoids as a function of aspect ratio from this much simpler, one-dimensional random jamming problem. A mean field treatment of the parking problem would suggest that, for monodisperse cars of length  $L$ , the largest space left unfilled between cars would be slightly smaller than  $L$ . The average space between cars is then  $L/2$ , and the average coverage,  $\text{car}/(\text{car} + \text{space})$  is  $L/(L + L/2) = 2/3$ . The exact solution is higher at 0.749.<sup>15,26</sup> We can now ask what happens when the cars are bidisperse with two lengths, as in the semimajor and semiminor axes of our m&m’s. Does the coverage increase or decrease? For small length differences  $L(1 \pm \epsilon)$ , the mean field treatment would give a maximum space of  $L(1 - \epsilon)$ , an average space of  $L(1 - \epsilon)/2$ , an average car length of  $L$ , and an average coverage of  $(2/3)(1 + \epsilon/3)$ . The density increases in a cusplike manner in terms of the ratio of the two lengths. The exact solution to the bidisperse parking problem has been published in ref 27, and the coverage indeed increases in a cusplike manner in the length ratio. A related polydispersity problem, the volume fraction at which the pressure of a polydisperse hard-sphere liquid diverges, also shows a linear increase from  $\phi = 0.64$  as polydispersity is increased.<sup>2</sup>

Our simulation of the bidisperse parking problem is shown in Figure 4. Selection of either size is equally probable. As in the random ellipsoid packing problem, there is a singularity at ratio 1 and an increase in packing fraction/coverage with size ratio  $\alpha$ . So it may be that the increase comes from the additional degree of freedom (in choice of size for the bidisperse case or orientation for ellipsoids) and the cusp is a consequence of being in a critical, terminal, or jammed random state.<sup>28</sup> Unlike the bidisperse parking problem which increases and saturates with



**Figure 4.** Simulations of two parking problems along a curb. The bidisperse system has two lengths,  $a$  and  $b$ . Selection of  $a$  or  $b$  is equally probable. The “Paris” parking problem is ellipses of aspect ratio  $b/a$  randomly oriented with their centers on the curb.

### “Paris” Parking Problem - Ellipses



**Figure 5.** Some typical configurations for the “Paris” parking problem. Low angle parking of long ellipses shows pronounced excluded volume effects.

length ratio, the ellipsoid packing has a maximum and then rapidly decreases with aspect ratio  $\alpha$ . Simulations on spherocylinders led Williams and Philipse to propose that this is an

excluded volume effect, that long objects have a certain volume but exclude a much larger volume from occupancy by neighboring particles. We can mimic this behavior in what we refer to as the “Paris parking problem”: there is a curb, and a parked car must have its center over the curb, but the angle with the curb can be random. Here we take an ellipse, choose a random orientation, and attempt to place the ellipse center at a random point on a line with no overlap with previously placed ellipses. Some particular configurations are illustrated in Figure 5, where it is clear that there are strong exclusion effects for high aspect ratios. We take the coverage as the length of the line covered by the ellipse itself, not the projection. The results of the simulation are shown in Figure 4. Here we see that the initial cusp and increase are present as for the bidisperse case, but for large aspect ratios, excluded volume dominates and the coverage decreases.

### Penny Packing

Because the initial experiments on ellipsoid packing were done with m&m’s, they received worldwide coverage in the media, and this elicited many comments from the scientific community as well as the general public. The usual comment from both scientists and the public was “Of course m&m’s pack better than spheres, they are like pennies thrown into a jar. They lie flat and pack like pancakes.” There are several things wrong with these arguments, which are worth pointing out. If the m&m’s were all to lie flat, then a simple affine expansion perpendicular to the flat plane would make them into spheres and their densest packing would be exactly the same as for spheres. The basic misconception is that pennies are flat cylinders and cylinders do pack better than spheres, at least in a crystalline array. Crystal packing of spheres is 74% and that of cylinders is 91%. However, an ellipsoid can, at best, only fill 2/3 of a cylinder, making the analogous crystal packing only 61%, less than even random sphere packing. Of course, we also experimentally verified that the m&m’s (and the simulated packings) were not orientationally ordered.<sup>11</sup> Finally it is interesting, for the sake of argument, to find out what a typical penny packing is like. A picture of a typical “random” penny jar accumulated over several years is shown in Figure 6. There is no doubt that, in this case, there are strong correlations



**Figure 6.** Typical configuration of pennies tossed “randomly” in a container (courtesy of Matt Sullivan). The central region has a packing fraction of  $0.574 \pm 0.005$ .

between orientations of close particles. The only sense in which these pennies are random is the way they were thrown in the jar.

There are important effects that we are not accounting for in this preliminary study. For example, it is important to note that a penny is not a circular cylinder (of small aspect ratio) but rather is a nonconvex solid object. Very little is known about the packing of nonconvex objects. It is clear, however, that certain nonconvex solids will have unusually low densities compared to those of convex objects. Moreover, the degree to which friction between the pennies is inhibiting densification has not been examined. Nonetheless, out of curiosity, we measured the packing fraction. We determined the amount of water needed to fill the container to different heights, and the average value for the 3000 pennies was 57%, considerably lower than that for random sphere packing. A more random packing of flat cylinders with the aspect ratio of pennies would be much lower.

## Summary

The ancient problem of random and ordered packing of hard objects continues to make contributions to mathematics, science, and engineering. The newly discovered results on ellipsoid packing open a new chapter in that study and, as presented above, raise as many questions as they answer. Among the most fundamental is whether objects can be found where the random packing is denser than the ordered packing and how such objects will behave thermodynamically. The inclusion of additional rotational degrees of freedom also brings to question the ideas of isostaticity and the stability of piles of particles. An interesting aspect of these problems is the cooperative nature of the research, which involves all of the tools at our disposal: experiments, models and model systems, theory, and simulation. This is an appropriate interplay that also reflects the research style of Bill Russel, to whom this volume is dedicated.

## Acknowledgment

It is a privilege to contribute an article to honor the career of Prof. Dean William B. Russel on the occasion of his 60th birthday. All of us have benefited from his research and have had fruitful collaborations with him. The first author of this note, P.M.C., has enjoyed the longest and most productive interactions with Prof. Russel. Together P.M.C. and W. B. Russel have shared a colloid group in the material institute at Princeton, joint between Physics and Chemical Engineering, over the past 15 years. Thanks to Prof. Russel, this group has been very successful in producing many exciting contributions to colloidal systems.

## Literature Cited

- (1) Zhu, J.; Li, M.; Meyer, W.; Ottewill, R. H.; STS-73 Space Shuttle Crew; Russel, W. B.; Chaikin, P. M. Crystallization of hard-sphere colloids in microgravity. *Nature* **1997**, *387*, 883.
- (2) Phan, S.-E.; Zhu, J.; Russel, W. B.; Chaikin, P. M. Phase transition, equation of state, and limiting shear viscosities of hard sphere dispersions. *J. Chem. Phys.* **1998**, *108*, 9789.
- (3) Russel, W. B.; Saville, D. A.; Schowalter, W. R. *Colloidal Dispersions*; Cambridge Monographs on Mechanics and Applied Mathematics; Cambridge University Press: Cambridge, U.K., 1989.
- (4) Bernal, J. D. Geometrical Approach to the Structure of Liquids. *Nature* **1959**, *183*, 141; The Bakerian Lecture, 1962. The Structure of Liquids. *Proc. R. Soc. London, Ser. A* **1964**, *280*, 299.
- (5) Pusey, P. N. Colloidal suspensions. In *Liquids, freezing and the glass transition*; Hansen, J. P., Levesque, D., Zinn-Justin, J., Eds.; Elsevier: Amsterdam, 1991; Chapter 10.

(6) Chaikin, P. M. Thermodynamics and Hydrodynamics of Hard Spheres; the role of gravity. In *Soft and Fragile Matter, Nonequilibrium Dynamics, Metastability and Flow*; Cates, M. E., Evans, M. R., Eds.; Institute of Physics Publishing: London, 2000; pp 315–348.

(7) Adler, B. J.; Wainwright, T. E. Phase transition for a hard sphere system. *J. Chem. Phys.* **1957**, *27*, 208–1209.

(8) m&m's candies are a registered trademark of Mars, Inc.

(9) Man, W.; Donev, A.; Stillinger, F. H.; Sullivan, M. T.; Russel, W. B.; Heeger, D.; Inati, S.; Torquato, S.; Chaikin, P. M. Experiments on Random Packings of Ellipsoids. *Phys. Rev. Lett.* **2005**, *94*, 198001.

(10) Torquato, S.; Trusket, T. M.; Debenedetti, P. G. Is Random Close Packing of Spheres Well Defined? *Phys. Rev. Lett.* **2000**, *84*, 2064.

(11) Donev, A.; Cisse, I.; Sachs, D.; Varioano, E. A.; Stillinger, F. H.; Connelly, R.; Torquato, S.; Chaikin, P. M. Improving the Density of Jammed Disordered Packings. *Science* **2004**, *303*, 990.

(12) Note that the data in Figure 1 are more recent than those in ref 11 and tend to show a very similar behavior for oblate and prolate spheroids.

(13) Alexander, S. Amorphous solids: their structure, lattice dynamics and elasticity. *Phys. Rep.* **1998**, *296*, 65.

(14) Edwards, S. F.; Grinev, D. V. Statistical Mechanics of Stress Transmission in Disordered Granular Arrays. *Phys. Rev. Lett.* **1999**, *82*, 5397.

(15) Torquato, S. *Random Heterogeneous Materials: Microstructure and Macroscopic Properties*; Springer: New York, 2002.

(16) Torquato, S.; Stillinger, F. H. Multiplicity of Generation, Selection, and Classification Procedures for Jammed Hard-Particle Packings. *J. Phys. Chem.* **2001**, *105*, 11849. Torquato, S.; Donev, A.; Stillinger, F. H. Breakdown of elasticity theory for jammed hard-particle packings: conical nonlinear constitutive theory. *Int. J. Solids Struct.* **2003**, *40*, 7143.

(17) Williams, S. R.; Philipse, A. P. Random packings of spheres and spherocylinders simulated by mechanical contraction. *Phys. Rev. E* **2003**, *67*, 051301.

(18) Andersen, H. C.; Chandler, D.; Weeks, J. D. Roles of Repulsive and Attractive Forces in Liquids: The Equilibrium Theory of Classical Fluids. *Adv. Chem. Phys.* **1976**, *34*, 105. Weeks, J. D.; Chandler, D.; Andersen, H. C. Relationship between the Hard-Sphere Fluid and Fluids with Realistic Repulsive Forces. *J. Chem. Phys.* **1971**, *54*, 5237.

(19) Torquato, S.; Stillinger, F. <http://arxiv.org/abs/math.MG/0508381>.

(20) Schilling, T.; Frenkel, D. *Comput. Phys. Commun.* **2005**, *16*, 9117.

(21) Donev, A.; Stillinger, F. H.; Chaikin, P. M.; Torquato, S. Unusually Dense Crystal Packings of Ellipsoids. *Phys. Rev. Lett.* **2004**, *92*, 255506.

(22) Donev, A.; Torquato, S.; Stillinger, F. H.; Connelly, R. Jamming in hard sphere and disk packings. *J. Appl. Phys.* **2004**, *95*, 989.

(23) This derivation came from discussions with Dr. Deniz Ertas.

(24) The two-dimensional ellipse is a good illustration of the difference between a jammed state and a state with no “zero modes”. A packing is jammed if any motion of the particles introduces overlap.<sup>15,16</sup> A “zero mode” invokes elasticity and suggests a linear response. A mode is soft (zero) if a displacement of the particles by a small distance  $\epsilon$  causes the distance between all particles to change by an amount  $O(\epsilon^2)$ . The three contact ellipse in Figure 3b has contact normals meeting at a common point. A rotation of order  $\epsilon$  applied to the center ellipse around this point will cause the distance between the particles to decrease by  $O(\epsilon^2)$ . Since the decrease causes overlap, the configuration is jammed. Since the response is quadratic rather than linear, there is a zero mode. (The restoring force in an elastic problem would not be proportional to the displacement and the frequency of this mode would be zero, unless the configuration is prestressed [Donev, Connelly, Stillinger, Torquato **2006**, in preparation]). To have no zero modes, four contacts would be needed, as in the work of Alexander.<sup>13</sup>

(25) Lubachevsky, B. D.; Stillinger, F. H. Geometrical Properties of Random Disk Packings. *J. Stat. Phys.* **1990**, *60*, 561.

(26) Renyi, A. *Publ. Math.* **1958**, *3*, 109. Gonzalez, J. J.; Hemmer, P. C.; Hoye, J. S. Cooperative Effects in Random Sequential Addition. *Chem. Phys.* **1974**, *3*, 288.

(27) Hassan, M. K.; Schmidt, J.; Blasius, B.; Kurths, J. Jamming coverage in competitive random sequential adsorption of a binary mixture. *Phys. Rev. E* **2002**, *65*, 045103.

(28) The cusp behavior appears to be intimately related to the “randomness of the packing and the type of singularity (i.e., exponent) may depend on the nature of the terminal state.

Received for review January 9, 2006  
Revised manuscript received April 8, 2006  
Accepted April 11, 2006