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## Multi-sized Sphere Packing in Containers: Optimization Formula for Obtaining the Highest Density with Two Different Sized Spheres

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This article provides a mathematical formula for determining the optimal sizes of two different sized spheres to maximize the packing density when randomized loose packing is employed in containers with various shapes. The formula was evaluated with numerous computer simulations involving over a million of spheres.

### 1. Introduction

This section introduces the motivation and purposes of this work. Some mathematical background is also presented to support later sections, which focus on building a model that matches the demands of the problem.

Concrete contains numerous pores that allow corrosion when chloride ions seep through the pores and make contact with the metal reinforcement. To protect the reinforcement in the concrete from the chlorides we can use an electric current to force nanoparticles into the pores to block access through them. This is called electrokinetic nanoparticle (EN) treatment. Also, replacing the air or water present in the pores in a block of concrete with solid materials or nanoparticles greatly improves the compressive strength of the concrete.

Two different sizes of nanoparticles are used in EN treatment. The smaller ones are used to block chloride ions and the larger ones to carry the smaller ones towards deeper locations in the pores. The larger nanoparticles also provide a rapid source of strength enhancement and general porosity reduction throughout the concrete material. This helps slow down the migration of chlorides that come

from the outside surface of the concrete. In fact, using only small nanoparticles seems to be inefficient for treatment purposes since their small size makes them too unstable to exist in anything but very dilute concentrations. EN treatments with such dilute concentrations require too much time to complete.

From a mathematical point of view, using two different sizes of nanoparticles to increase the general packing density throughout the pore structure is reasonable as smaller spheres can fit into spaces left by the packing of mono-sized spheres. This improves porosity reduction since packing two different sizes of spheres in the space yields a higher density than packing spheres of the same size. For example, it is well known that the highest density that can be achieved for identical sphere packing in unbounded space is  $\frac{\pi}{\sqrt{18}} = 0.74048$ . This means that 74% of the volume space is filled with solid material. This is the same as the density for the Face-Centered Cubic (FCC) crystal structure or the Hexagonal Close-Packed (HCP) crystal structure. However, if two sizes of sphere are used, theoretically the density can be increased to  $1 - (1 - \frac{\pi}{\sqrt{18}})^2 = 0.93265$ . This is because minimizing the size of the smaller spheres would increase the density in the remainder of the space after packing larger spheres.

Unfortunately the upper bound by this theory is much higher than densities that can be reached in practice since there is a certain limitation as regards the sizes of nanoparticles, and the nanoparticles must be put into bounded spaces and the packing must be random. Therefore a natural question to ask is what combination of large and small nanoparticles sizes will yield the highest density. We present a formula for the larger size of nanoparticles that will allow us to obtain the highest density when an arbitrary smaller size of nanoparticles is given. To accomplish this task, we need a simple model of nanoparticle packing and an approximate formula for the packing density.

The main purposes of this work are to introduce a simple model that faithfully represents two-sized nanoparticle packing, and to give a simple and good formula approximating its packing density.

The following sections present a model for packing two sizes of spheres into a container. Also, we investigate the most important issue, namely the boundary evacuation effect, which does not arise in the traditional sphere packing problem.

In Section 2, we propose a new packing model with pits and quasi-pits. This

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model reproduces nanoparticle filling where intermolecular force has a greater influence than gravity. Section 3 investigates the packing density with mono-sized spheres in an arbitrary container. The boundary evacuation effect is introduced and a formula is presented that provides an approximate value for the packing density. This formula involves only the surface-volume ratio of the container and the radius of the spheres, nevertheless it gives good approximate values for containers of various shapes. In Section 4, we investigate the packing density with two sizes of sphere in an arbitrary container. A formula is presented that gives an approximate value for the packing density with two sizes of spheres. This formula provides a solution to the nanoparticle packing problem for the pair of nanoparticle sizes that yield the highest density. Section 5 presents a number of numerical experiments and examines the approximation formula of the packing density for various shapes of containers. In the last section, we apply the approximation formula to the density of nanoparticles in capillary pores in concrete.

## 2. Computational Packing Model for Nanoparticles

In this section, a computational sphere packing model is introduced and its advantages are explained and it is compared with other existing models. The model uses both “pits” and “quasi-pits”, which are defined later, to present a packing model for nanoparticles that is as close as possible to reality.

In 1969, identical steel balls were packed randomly and this was called random close packing (RCP) since the container was shaken after being filled with steel balls. The experiment for one size of steel sphere RCP yielded a density of about 64%<sup>1)</sup> and relied on the fact that the spheres would rearrange themselves into a more dense structure under the force of gravity combined with the force of shaking. In the experiments, gravity acts in only one direction from the top to the bottom and governs the entire experiments except for the shaking.

Packing affected by a one-directional force, such as gravity, results in a higher density than packing without a specific force direction. This does not apply in our case since gravity affects nanoparticles much less than the intermolecular forces that operate between nanoparticles. To emphasize the fact that we do not apply additional force by shaking the container, we refer to the model described

in this article as the Random Loose Packing Model (RLP).

There is always a dilemma when we attempt to create a computer model to calculate or simulate the random packing of spheres. The problem is to keep the randomness as close as possible to reality, and also complete the packing process in a reasonable amount of time. These factors are indicated by the number of nanoparticles that a model can handle in a certain period of time.

To meet the two requirements of high speed and closeness to reality, we propose the new concepts of a pit point and a quasi-pit point, and we define them in this section. Our model is superior not only because it can handle an enormous number of nanoparticles but also because it can provide results much more quickly than previous models, for example those shown in Refs. 2) and 3).

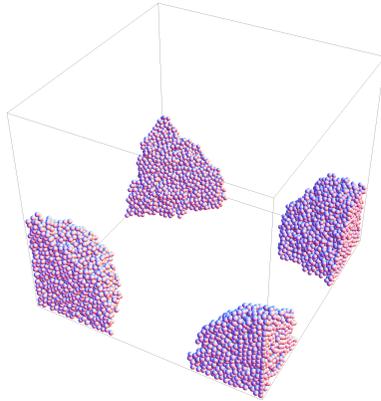
In this section, let  $r$  be the radius of the packing spheres.

- We call the center of a sphere of radius  $r$  a *pit supported by three tangent points* if the sphere is tangential at the three points located on the boundary of the container or on the previously packed spheres, but is completely disjoint from the interior of any previously packed spheres.
- When using a uniform distribution, randomly selected points  $Q$  inside the container are called *quasi-pits* if  $Q$  is a distance  $r$  away from the surface of the container.
- The center of a newly packed sphere will be located at one of the pits or quasi-pits, which will be selected at random.

A pit as defined above is the center of a sphere that is in contact with the container or other spheres at three points on the surfaces of the container or previously packed spheres. In other words, pits are the centers of newly packed spheres that are in contact with the surface of already settled spheres or the container surface at three points.

Many computerized random sphere packing experiments have been reported, and they used various concepts and definitions of pits. For example, see Refs. 4) and 5). pits are conducted.

If the container surface and packed sphere surfaces are completely smooth, and if special gravitation does not operate between the container surface and the packed spheres, it is proper to think that the next packed sphere is stabilized at the position where it comes into contact with three points on the container

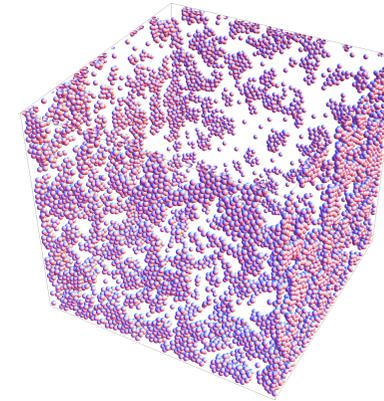


**Fig. 1** Packing of 10,000 spheres without quasi-pits.

surface and/or spheres that have been previously packed. However, with a real container and nanoparticles, it can be considered that the packed sphere may even be placed in a position where it touches only one point on the container surface, as a result of the intermolecular force or coulomb force acting on the container wall surface and particle and surface irregularities.

In the computational experiment that we undertook in this research, to reproduce the behaviors of nanoparticles by using pits and quasi-pits, we chose quasi-pits that were uniformly distributed in terms of density on the container surface. The distribution density of the quasi-pits is represented by the number  $\rho$  of quasi-pits per  $4\pi r^2$ , the surface area of the sphere. This is then used as a parameter for expressing the strength with which a nanoparticle is drawn across the inner surface of the container. With the computer experiment, we assumed that  $\rho = 1$ . It means that there is approximately 1 quasi-pit within a circle of radius  $2r$  on the container surface.

If there were no quasi-pits, for example with a cubic container, packing would begin with one of the pits around the corners of the container and the randomness would decrease (**Fig. 1**). However, if we use quasi-pits, packing starts when a random particle adheres to the container surface (**Fig. 2**).



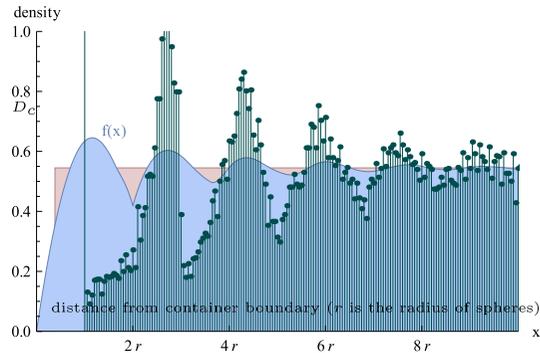
**Fig. 2** Packing of 10,000 spheres with quasi-pits.

### 3. Packing with Mono-sized Spheres

When identical spheres are randomly packed in a limited space or a container, the packing density is unlikely to be uniform. For example, the packing density in a region around the center of the space bounded by the container would not be the same as the density in a region close to the surface of the container. In this section, we discuss how to handle the difference between the packing densities for the center and the nearby container surface.

When spheres are packed in a container, it is a reasonable assumption that the density in a region far from the container surface (by comparison with  $r$ , the radius of the packing spheres) is independent of the shape of the container. This former density will be called the *center part density*, and is denoted by  $D_c$ . A number of computational experiments have been performed with various shapes and sizes of containers and different sizes of spheres, and  $D_c$  has been estimated by  $D_c = 0.543 \pm 0.002$ .

However, the packing density near the surface of the container does not coincide with  $D_c$ , because of the evacuation of the packed spheres at the container surface and because the number of spheres are tangential to the container surface. **Figure 3** shows the packing density near a container surface (blue colored area) and  $D_c$  (pink colored rectangular area) and a histogram of distances between the



**Fig. 3** Packing density distributions obtained from computational experiments.

centers of the packed spheres and the container surface (green vertical lines). The  $y$  axis of the histogram is normalized to the packing density, that is, the number of spheres times the sphere volume over the container volume corresponds to the each bin of the histogram. Here,  $r$  on the horizontal axis is the radius of the packed spheres.

The packing density function  $f(x)$  in Fig. 3, where  $x$  is the distance from the container surface, oscillates and converges with the center part density  $D_c$ . The integrated value of  $f(x)$  is slightly smaller than that of  $D_c$ . We can consider the difference  $\frac{1}{D_c} \int_0^\infty (D_c - f(x))dx$  to be the boundary evacuation effect of the container. In Fig. 3, the pink colored area that represents  $D_c$  does not reach the  $y$ -axis and the gap represents the boundary evacuation effect, so the area below the line coincides with the area below the curve of  $f(x)$ . The boundary evacuation effect is in proportion to the packed sphere radius  $r$ , and the proportional coefficient

$$\epsilon = \frac{1}{rD_c} \int_0^\infty (D_c - f(x))dx \quad (1)$$

is called the boundary evaluation coefficient. From a number of numerical experiments, it is estimated that  $\epsilon = 0.387 (\pm 0.01)$ , which increases with the quasi-pit distribution density  $\rho$  but does not depend on the shape and size of the container.

When spheres of radius  $r$  are packed in a container of volume  $V$  and surface area  $S$ , the boundary evacuation effect ranges over a region within a distance  $\epsilon r$

from the surface of the container, whose volume is approximately  $\epsilon rS$ . And we can consider that the remaining volume  $V - \epsilon rS$  of the container is filled with spheres with a density  $D_c$ . Thus, we obtain the following approximate formula for the total packing density  $D$

$$D = \frac{(V - \epsilon rS)D_c}{V} = (1 - \epsilon rS/V) D_c \quad (2)$$

The surface-to-volume ratio  $S/V$  in this formula is one of the most important parameters representing the shape and scale of an object. It takes a small value when the object is roughly spherical and its scale is large. For example,  $S/V = \frac{3}{r}$  for a sphere of radius  $r$ , and  $S/V = \frac{6}{a}$  for a cube of edge length  $a$ .

Since the approximation Eq. (2) involves only the surface-to-volume ratio  $S/V$ , we do not have to know exact shapes to optimize the ratio of two different sizes of spheres. As we see in Section 5, if the containers or the pores in concrete have a non-convex shape, then  $S/V$  is large and spheres of smaller size will optimize the density.

#### 4. Packing with Two Sizes of Spheres

In this section, we discuss packing spheres of two different sizes in containers. We employ a sequential rather than simultaneous packing method in that we pack the larger spheres first and then pack the smaller spheres into the remaining space inside the container.

Let  $r_1$  and  $r_2$  be the radii of the two sizes of spheres to be packed and  $r_1 < r_2$ . Let  $V$  and  $S$  be the volume and surface area of the container, respectively. We first pack the spheres of radius  $r_2$ . From the approximating Eq. (2), we derive the following approximate density  $D_2$  of the packed spheres of radius  $r_2$

$$D_2 = (1 - \epsilon r_2 S/V) D_c. \quad (3)$$

The total volume of the packed spheres is therefore approximately  $(V - \epsilon r_2 S) D_c$  and the total area of the spheres is  $\frac{3}{r_2} (V - \epsilon r_2 S) D_c$ .

Next, we fill the remaining space around the already packed larger spheres inside the container, whose volume is  $V - (V - \epsilon r_2 S) D_c$  and whose surface area is  $S + \frac{3}{r_2} (V - \epsilon r_2 S) D_c$ . By applying the formula for approximating the packing density (2), the total volume of radius  $r_1$  is  $D_c (V - (V - \epsilon r_2 S) D_c - \epsilon r_1 (S +$

$\frac{3}{r_2}(V - \epsilon r_2 S)D_c$ ), and its approximate density in the container is

$$D_1 = D_c(1 - D_c - 3\epsilon D_c \frac{r_1}{r_2} + (D_c r_2 - (1 - 3\epsilon D_c)r_1)\epsilon S/V). \tag{4}$$

Then, the total packing density  $D_{1,2}$  of the two sizes of sphere is approximated by

$$D_{1,2} = D_c(2 - D_c - 3\epsilon D_c \frac{r_1}{r_2} + ((D_c - 1)r_2 - (1 - 3\epsilon D_c)r_1)\epsilon S/V) \tag{5}$$

If we fix  $r_1$  and vary  $r_2$ , then  $D_{1,2}$  takes the maximum value

$$D_{1,2}^{(\max)} = D_c(2 - D_c - \epsilon(1 - 3\epsilon D_c)r_1 - 2\epsilon\sqrt{3(1 - D_c)r_1 S/V}) \tag{6}$$

at

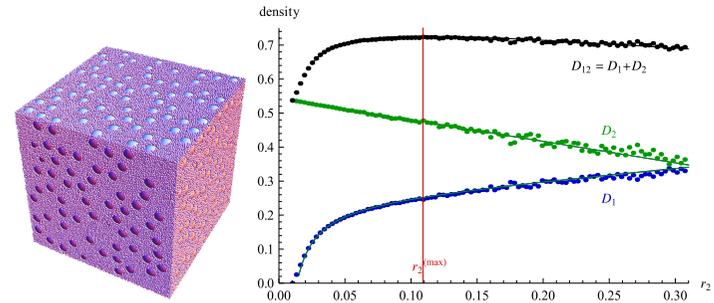
$$r_2^{(\max)} = \sqrt{\frac{3D_c r_1}{(1 - D_c)S/V}}. \tag{7}$$

This is a solution for the two sizes of nanoparticle that yield the highest density when the size of the smaller nanoparticle is given.

### 5. Numerical Experiments

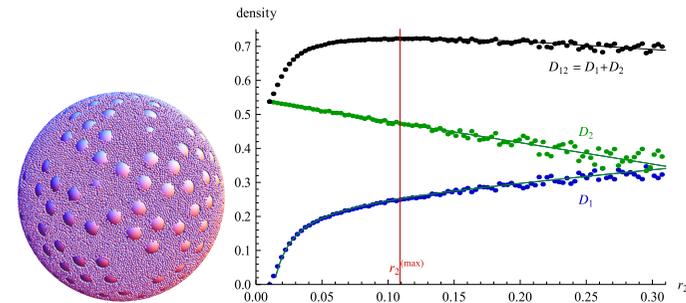
In this section, we present experimental results for packing spheres of two different sizes into containers of several shapes. In each experiment, the radius  $r_1$  of the smaller spheres was fixed at  $r_1 = 0.01$  and the radius  $r_2$  of larger spheres was varied by  $0.01 < r_2 < 0.3$ . The actual measured values of the numerical experiments are shown by dots and the value of the approximating formulae for the densities  $D_1, D_2$  of the two sizes of sphere and the total density  $D_1 + D_2 = D_{1,2}$  are shown by the curved lines. The vertical line shows the radius  $r_2^{(\max)}$  of the larger spheres, which increases the total density at  $D_{1,2}^{(\max)}$ .

**Figure 4** shows a packing experiment in cubic container with dimensions of  $2 \times 2 \times 2$ , whose surface-volume ratio is 3. **Figure 5** shows a packing experiment in a spherical container with a radius of 1, whose surface-volume ratio is 3. Note that, since these two containers have the same surface-volume ratio, their



**Fig. 4** Cubic container ( $S/V = 3$ ).

$$D_{1,2} = 0.7888 - \frac{0.003423}{r_2} - 0.2881r_2, \\ r_1 = 0.01, \quad r_2^{(\max)} = 0.109, \quad D_{1,2}^{(\max)} = 0.726$$

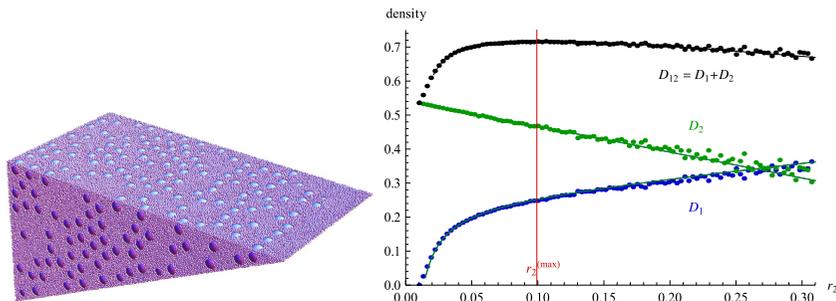


**Fig. 5** Spherical container ( $S/V = 3$ ).

$$D_{1,2} = 0.7888 - \frac{0.003423}{r_2} - 0.2881r_2, \\ r_1 = 0.01, \quad r_2^{(\max)} = 0.109, \quad D_{1,2}^{(\max)} = 0.726$$

approximating formulae coincide. **Figure 6** shows a packing experiment in a prism container with a right triangular base whose dimensions are  $2 \times 4$  and height 2, and whose surface-volume ratio is 3.62. **Figure 7** shows a packing experiment in a dented spherical container where the ball of radius 1 is dented at the north and south poles with a radius of 1. Since the surface-volume ratio of 8 of the dented spherical container is much larger than that of previously reported containers,  $r_2^{(\max)}$  and  $D_{1,2}^{(\max)}$  are smaller than with previous containers.

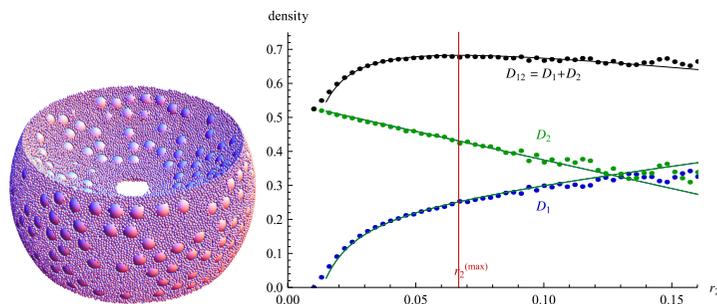
In each experiment, the actual measured values of the densities differ from the approximation when  $r_2$  becomes as large as one-severalth of the container diameter, nevertheless the formula provides a good approximation. The root mean square  $Err_{RMS}$  of the difference between the actual measurement and the approximation in the entire range of  $r_2$  is 0.014, whereas  $Err_{RMS} = 0.0045$  if the  $r_2$  range is restricted to the neighborhood of  $r_2^{(max)}$ ,  $\frac{1}{2}r_2^{(max)} < r_2 < 2r_2^{(max)}$ .



**Fig. 6** Prism container ( $S/V = 3.62$ ).

$$D_{1,2} = 0.7883 - \frac{0.003423}{r_2} - 0.3475r_2,$$

$$r_1 = 0.01, \quad r_2^{(max)} = 0.099, \quad D_{1,2}^{(max)} = 0.7191$$



**Fig. 7** Dented spherical container ( $S/V = 8$ ).

$$D_{1,2} = 0.7849 - \frac{0.003423}{r_2} - 0.7683r_2,$$

$$r_1 = 0.01, \quad r_2^{(max)} = 0.068, \quad D_{1,2}^{(max)} = 0.6824$$

## 6. Application to EN Treatment and Summary

This section presents an application to electrokinetic nanoparticle treatment and a summary.

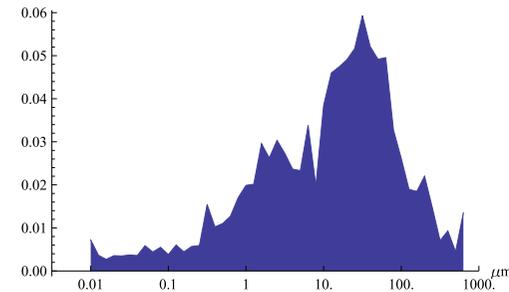
Capillary pores in concrete interconnect to form a capillary pore system that allows both water flow and ionic diffusion. **Figure 8** shows the distribution of the diameter of capillary pores in concrete<sup>6)</sup>.

A long cylinder of radius  $r$  has a surface-volume ratio  $S/V = \frac{2}{r}$ , nevertheless a capillary pore of radius  $r$  in concrete appears to have a much larger surface-volume, because its surface is rough and uneven as shown in **Fig. 9**. Therefore, we assume that the surface-volume ratio of capillary pores of radius  $r$  is  $\frac{10}{r}$ . Under this assumption, by applying the approximation formula, the packing density of radius  $r_1$  and  $r_2$  spheres into capillary pores that are distributed as in Fig. 8 is

$$D_{1,2} = 0.791 - 4.06r_1 - 0.342\frac{r_1}{r_2} - 5.02r_2,$$

where the unit of length is  $\mu\text{m}$ . Actually, nanoparticles of radius  $r_1 = 0.001 \mu\text{m}$  and  $r_2 = 0.01 \mu\text{m}$  are used for the electrokinetic nanoparticle treatment, and in this actual case  $D_{1,2} = 0.703$ . If the radius of the smaller nanoparticles is fixed at  $r_1 = 0.001 \mu\text{m}$ ,  $D_{1,2}$  takes a maximum value of 0.704 when the radius of the larger nanoparticles is  $r_2 = 0.00826$ . Therefore, the pair of nanoparticles that is actually used is close to the most suitable case.

The approximation Eqs. (2) and (5) involve only the surface-volume ratio  $S/V$  of the container and the radii of the packing spheres, nevertheless those formulae



**Fig. 8** Distribution of capillary pore diameters in concrete<sup>6)</sup>.

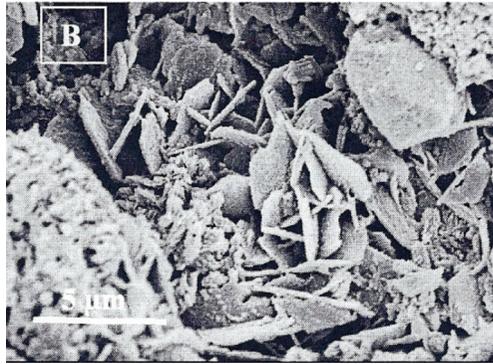


Fig. 9 Photograph of pore surface in concrete<sup>6)</sup>.

give very good approximations of the packing density. To yield these formulae, the volume of the region within distance  $\epsilon r$  is approximated by  $\epsilon r S$ . If the degree of this approximation is increased using the mean curvature and the Gaussian curvature of the container surface, the formulae become complicated but do not provide appreciably better approximations.

One of the next goals is to investigate what will happen if we pack spheres of two different sizes simultaneously, instead of packing larger spheres first and smaller ones later. Also we want to know what will happen if we pack spheres of more than two different sizes into containers. To our knowledge, using quasi-pits to model forces among molecules is new. We will seek other models and simulations to fit the behaviors of nanoparticles since many potential medical applications have already been investigated, but nanoparticles are still too expensive to waste on random experiments.

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