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Random close packing fractions of lognormal distributions of hard spheres

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ABSTRACT

We apply a recent one-dimensional algorithm for predicting random close packing fractions of polydisperse hard spheres [Farr and Groot, J. Chem. Phys. 133, 244104 (2009)] to the case of lognormal distributions of sphere sizes and mixtures of such populations. We show that the results compare well to two much slower algorithms for directly simulating spheres in three dimensions, and show that the algorithm is fast enough to tackle inverse problems in particle packing: designing size distributions to meet required criteria. The one-dimensional method used in this paper is implemented as a computer code in the C programming language, available at http://sourceforge.net/projects/spherepack1d/ under the terms of the GNU general public licence (version 2).

1. Introduction

In granular and mesoscopic systems, various material properties depend on the close packed volume fraction of the constituent particles. For example, in the Krieger–Dougherty [1] relation

$$\eta_r = (1-\phi/\phi_{max})^{-[\eta]\phi_{max}}, \quad (1)$$

used for estimating the viscosity of a suspension of hard particles in a Newtonian solvent [where η_r is the viscosity relative to that of the solvent, ϕ the volume fraction of the particles and $[\eta]$ a number (equal to 2.5 for spheres)], the viscosity is predicted to diverge at the packing fraction ϕ_{max}. The value of ϕ_{max} may correspond to a random arrangement at low shear rates or an aligned 'string phase' at high shear rates [2,3], but in either case, Eq. (1) implies that this quantity influences the viscosity over the whole range of volume fractions. On the other hand, deformable particles may be packed above the Kreiger–Dougherty ϕ_{max}, and their material properties, such as yield stress [4,5], can be deduced from how far above close packing the system lies.

For many colloidal and granular systems, the constituent particles do not form regular, crystalline arrays, but instead are rather randomly arranged when a jammed state is reached, which represents a close packed arrangement. The concept of random close packing ('RCP') was first clearly described for monodisperse smooth hard spheres by Bernal and Mason [6], and the packing of smooth spheres remains an important approximation for less ideal systems.

For the monodisperse case, there has been controversy over the definition (and even existence [7]) of RCP, as crystallization to a face centred cubic arrangement [8,9] is possible when sufficient opportunity to explore the configuration space is allowed. Theoretical work on random jammed states [10] has clarified these issues, but the simplest evidence for a well-defined RCP state is that different packing algorithms generally converge to statistically very similar configurations and packing fractions. One can therefore define RCP operationally, as the outcome of such a packing algorithm. Various algorithms have been explored: Conceptually the simplest is the Lubachevski–Stillinger ('LS') algorithm [11] in which spheres at a low volume fraction are placed in a box with periodic boundary conditions, by random sequential addition. They are then given random initial velocities and permitted to move and collide elastically while their radii grow at a rate proportional to their initial radius, until a jammed state is reached. This algorithm takes three input parameters: the number of spheres N_s, the initial volume fraction ϕ_{init} and the ratio δ of the radial growth rate to the initial particle size. For large N_s, the final packing fraction is only very weakly dependent on δ and ϕ_{init}. Usually fairly large values (around $\delta = 0.1$) are chosen, to avoid local crystalline regions. Even with efficient methods for identifying neighbours however, the LS algorithm converges rather slowly to the jammed RCP state because of the diverging number of collisions as this point is approached.

Other authors have therefore modified the dissipative particle dynamics [12] method and simulated smooth, soft (Hertzian) spheres, with radial dissipative forces. In the limit of zero confining pressure, these also behave as hard spheres and give extremely similar results to the LS algorithm, although the amount of radial dissipation (or equivalently the particle size) does have a very weak effect on the final RCP volume fraction [13].

In moving toward more realistic systems, there are three constraints in the above-mentioned models which one can imagine removing: the smoothness of the particles (that is to say lack of sliding friction), their spherical shape, and monodispersity.

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We note in passing that monodisperse hard spheres, but with the addition of sliding friction, have been considered in the literature, and this leads to a family of randomly packed states [14], with RCP (applying to smooth spheres) and random loose packing (highly frictional spheres) being the extreme ends of this spectrum. Corresponding packing fractions are in the range 0.64 to 0.53. We also note that RCP of non-spherical, but smooth particles have also been extensively studied; for example in Ref [15], different smooth superelliposids are taken as the objects to be packed.

However, the work reported here will cover only the case of polydisperse smooth spheres. A certain amount of theoretical effort has been devoted to this area, notably Refs. [16–18]. The last of these appears to provide a flexible approximation scheme that could be applied to fairly general size distributions; although the authors note that for bidisperse sphere size ratios greater than 2, the accuracy declines. Despite these advances, all the theoretical approaches are to some extent heuristic, requiring comparison to numerical data. Therefore the most obvious route forward, which is to generalize the numerical packing algorithms that were developed for the monodisperse case, remains necessary. In the present paper, the two sets of 3d simulation results we present are based on a hard sphere method (a modification of the LS algorithm [19]) and a soft particle ('SP') algorithm (taken directly from Ref. [13]).

However, all these direct simulation methods are computationally rather expensive, typically taking hours or days to obtain high quality results. Not only is it inconvenient to have to bring to bear a complex and expensive algorithm when one may only be interested in the random packing of a relatively simple size distribution, but the slow time for solution makes solving inverse problems infeasible. By an 'inverse problem' we mean searching for a size distribution which satisfies certain packing criteria, such as finding the largest RCP volume fraction given a fixed minimum and maximum size for the particles, or other problems of a similar nature.

Recently however, a quick and apparently quite accurate algorithm [13] has been described which attempts to approximate the RCP fraction of any distribution of sphere sizes, by mapping the problem onto a one dimensional system of rods. This can allow the RCP volume fraction to be obtained in around one second (see Table 1), and therefore makes routine evaluation of these numbers relatively easy. However, some care is required to implement the algorithm for general distributions of sphere sizes, and no reference implementation code has hitherto been published.

This paper therefore aims to demonstrate that this one dimensional 'rod-packing' (RP) algorithm can be implemented efficiently for typically encountered sphere size distributions, and also to compare the results to the more traditional direct simulation approaches above for calculating RCP volume fractions.

2. Log-normal size distributions

2.1. Analysing experimental data

Consider a distribution of sphere sizes. Let the number-weighted distribution of diameters be given by $P_{3d}(D)$, so that the fraction of the number of spheres with diameters between D and $D + dD$ is $P_{3d}(D)dD$. The volume-weighted distribution of diameters will then be $P_{\mathrm{vol}}(D) \propto D^3 P_{3d}(D)$, while the surface- and diameter-weighted distributions will be respectively $P_{\mathrm{surf}}(D) \propto D^2 P_{3d}(D)$ and $P_{\mathrm{diam}}(D) \propto D P_{3d}(D)$.

For any such number-weighted size distribution $P_{3d}(D)$, one defines an m'th moment by

$$\mu_m \equiv \int_0^\infty D^m P_{3d}(D)\mathrm{d}D. \tag{2}$$

It is often the case that the volume-weighted mean diameter $d_{4,3}$ and the surface-weighted mean diameter $d_{3,2}$ are experimentally accessible. They are defined in terms of the moments via:

$$d_{4,3} \equiv \mu_4/\mu_3 \tag{3}$$

$$d_{3,2} \equiv \mu_3/\mu_2. \tag{4}$$

In studies of emulsions [20,21] it is frequently found that the volume-weighted size distribution of droplets is log-normal, and this can also be a good approximation for granular materials, such as sediments [22,23]. In general, if $P_{\mathrm{vol}}(D)$ is log-normal with a 'width' σ, it will have the form:

$$P_{\mathrm{vol}}(D) = \frac{1}{D\sigma\sqrt{2\pi}} exp\left\{ -\frac{\left[ln\left(D/D_{0,\mathrm{vol}}\right)\right]^2}{2\sigma^2} \right\}, \tag{5}$$

where $D_{0,\mathrm{vol}}$ is a reference diameter setting the scale. Performing the integrals of Eqs. (3) and (4), we see that

$$D_{0,\mathrm{vol}} = \left(d_{3,2} d_{4,3}\right)^{1/2}. \tag{6}$$

We note in passing that one could alternatively define a log-normal distribution with particle volume, rather than diameter, as the independent variable; in which case, for the same physical distribution, the volume-based lognormal width σ_v will be 3σ.

Returning to diameter as the independent variable, in experimental work it is usual to plot the volume-weighted diameter distribution on a logarithmic scale, showing the fraction of the spheres' volume per decade of diameter. If we define x as the base ten logarithm of the diameter measured in meters (so x counts the number of decades)

$$x \equiv log_{10}(D/\mathrm{m}), \tag{7}$$

$$x_0 \equiv log_{10}\left(D_{0,\mathrm{vol}}/\mathrm{m}\right), \tag{8}$$

then the distribution by decade corresponding to $P_{\mathrm{vol}}(D)$ is

$$P_{\mathrm{vol}}^{\mathrm{dec}}(x) \equiv \frac{dD}{dx} P_{\mathrm{vol}}(D) = \frac{ln(10)}{\sigma\sqrt{2\pi}} exp\left[-\frac{(x-x_0)^2}{2(\sigma/ln(10))^2} \right]. \tag{9}$$

We see that $P_{\mathrm{vol}}^{\mathrm{dec}}(x)$ has a simple normal distribution in x, and the full width (in decades) at half maximum is very close to σ itself (more precisely 1.023σ).

2.2. Weighted distributions

A little algebra shows that if $P_{\mathrm{vol}}(D)$ is log-normally distributed, then so are the number-, diameter- and surface-weighted distributions. That is to say they have exactly the same functional form as Eq. (5), with the same width σ, but different values of the reference diameter. For example the number-weighted diameter distribution is

$$P_{3d}(D) = \frac{1}{D\sigma\sqrt{2\pi}} exp\left\{ -\frac{[ln(D/D_0)]^2}{2\sigma^2} \right\}, \tag{10}$$

Table 1
Simulation times t in milliseconds for the RP algorithm applied to a lognormal distribution of spheres, implemented on a 3.2GHz Intel Pentium processor for various values of rod number N and width σ. The predicted RCP volume fraction is ϕ_{RP}.

σ	N	ϕ_{RP}	t/ms
0.0	16,000	0.643485	40
0.5	16,000	0.707259	479
1.0	16,000	0.801339	507
0.0	64,000	0.643485	331
0.5	64,000	0.707262	2151
1.0	64,000	0.801368	2644