Model of random packings of different size balls

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We develop a model to describe the properties of random assemblies of polydisperse hard spheres. We show that the key features to describe the system are (i) the dependence between the free volume of a sphere and the various coordination numbers between the species, and (ii) the dependence of the coordination numbers with the concentration of species; quantities that are calculated analytically. The model predicts the density of random close packing and random loose packing of polydisperse systems for a given distribution of ball size and describes packings for any interparticle friction coefficient. The formalism allows to determine the optimal packing over different distributions and may help to treat packing problems of non-spherical particles which are notoriously difficult to solve.

Understanding the basic properties of spheres packings is a major challenge since this problem may provide valuable knowledge regarding low temperature phases in condensed matter physics [1]. The canonical example is perhaps the monodisperse sphere packing problem. It has been mathematically proven that the optimum way to arrange monodisperse spheres is the face-centered cubic lattice; a problem that has been solved recently by Hales, ~ 400 years after the famous Kepler conjecture on the issue. On the other hand, it is commonly observed that packings arrange in a random fashion at a lower density state called random close packing or RCP [2]. Furthermore, packings are mechanically stable up to an even lower limit called random loose packing, RLP. In parallel with the large literature dealing with monodisperse sphere packings, a large body of experimental, theoretical and numerical work has been devoted to the analysis of polydisperse systems; the interest arising due to the simple fact that polydispersity is omnipresent in most realistic systems and industrial applications [3, 4]. While previous approaches have focused on frictionless packings, an integrated analytical approach that brings together different observations for all packings from RLP to RCP and for any friction or coordination number is still lacking. Based on our previous statistical mechanics approach [5], here we build such a framework.

We show that the key aspect to solve this problem is the dependence of the various coordination numbers between the different species and the concentration of the species. This is calculated here and shown to agree well with computer simulations. This result is then incorporated into a statistical theory of volume fluctuations as in [6] which calculates the free volume of a particle in terms of the coordination number. The main result is the prediction of the RLP and RCP limiting densities for a given distribution of ball sizes as well as the prediction of densities for any packing in between those limits. The formalism allows for a determination of the best packing fraction in terms of different distribution of ball sizes with specified constraints, as we show with a simple example. We discuss possible generalization of the method to solve more difficult problems like the phase behavior of systems of non-spherical particles like rods or spherocylinders in any dimensions; problems of long-standing history in condensed matter [6].

Recent theoretical advances [3] allow for the prediction of the density of RCP and RLP for equal-size ball packings using a relation between the average volume and the geometrical coordination number. Following this approach, we here describe long-range spatial correlations through a mean-field background term. This approximation makes the problem amenable to analytic calculations, and is shown to describe well our simulation results. An explicit inclusion of such correlations is possible in our framework, but severely complicates any solution attempts. Thus, we believe that the present approach is accurate enough for many important properties, such as the volume fraction calculation.

The above theoretical framework will guide the present formalism for polydisperse systems. We first treat the case of binary mixtures of hard spheres of radius \( R_1 \) and \( R_2 > R_1 \) in 3d and then generalize the problem to any distribution and dimension.

**Calculation of \( z_{ij} \).** — The key quantity to calculate is \( z_{ij} \), denoting the mean number of contacts of a ball of radius \( R_i \) with a ball of radius \( R_j \), versus the concentration of one of the species. We need a formula for \( z_{ij} \) as a function of \((z, x, \frac{R_i}{R_j})\), the later being the size ratio, \( x \) is the fraction of small balls in the packing \( x \equiv N_1/(N_1 + N_2) \) with \( N_i \) the number of \( i \) balls and \( z \) is the global geometrical coordination number averaged over all the particles: \( z \equiv x z_1 + (1-x) z_2 \) where \( z_i \) is the average coordination of each species.

The coordinates are determined by three equations:

\[
z_i = z_{i1} + z_{i2}, \quad (i = 1, 2), \quad x z_{12} = (1-x) z_{21}.
\]

We assume that these coordinations are inversely proportional to the average solid angle extended by contacting balls \( R_1 \) and \( R_2 \). The average solid angles are denoted \( \langle S_i^{\text{occ}} \rangle \) and are calculated in terms of the solid angle that a ball \( R_j \) occupy on a ball \( R_i \) according to
The classical Voronoi polyhedron defined by the center of the particle, one should consider all the points which are closer to the surface of a given particle. Such a construction is called the Voronoi S region and tiles a system of nonspherical convex particles and polydisperse systems as can be seen in Fig. 1b). Following this approach we calculate the average volume of a polydisperse Voronoi cell, denoted $W$. The volume fraction is given by $\varphi = \frac{V_g}{V_0}$, where $V_g = \frac{4\pi}{3}(xR_1^3 + (1-x)R_2^3)$ is the mean volume of a ball. We first find the analytical formula of the Voronoi S region. The boundary of the Voronoi cell in the direction $\hat{s}$ of a $i$ ball next to a $j$ ball at position $r_{ij}$ is (Fig. 1b):

$$l_{ij}(\hat{s}) = \frac{1}{2} \frac{r_{ij}^2 - (R_i - R_j)^2}{r_{ij}(\hat{r}_{ij} \cdot \hat{s}) - (R_i - R_j)}.$$

where $\hat{s}$ and $\hat{r}_{ij}$ are unitary. Thus, the boundary of a Voronoi cell of a ball $i$ in the direction $\hat{s}$ over all the particles $j$ for any $l_{ij}(\hat{s}) > 0$. This leads to

$$l_i(\hat{s}) = \frac{1}{2} \min_{\hat{s}, \hat{r}_{ij} > \frac{R_i - R_j}{r_{ij}}} \frac{r_{ij}^2 - (R_i - R_j)^2}{r_{ij}(\hat{r}_{ij} \cdot \hat{s}) - (R_i - R_j)}.$$

The volume of the cell of the ball $i$ is then given by $W_i = \frac{1}{4\pi} \int l_i(\hat{s})^3 d\hat{s}$. We define the orientational Voronoi volume, $W_i^s$, along the direction $\hat{s}$ by $W_i = \frac{1}{4\pi} \int W_i^s d\hat{s} = \langle W_i^s \rangle_{\hat{s}}$. This leads to

$$W_i^s = \frac{\pi}{6} \min_{\hat{s}, \hat{r}_{ij} > \frac{R_i - R_j}{r_{ij}}} \left( \frac{r_{ij}^2 - (R_i - R_j)^2}{r_{ij}(\hat{r}_{ij} \cdot \hat{s}) - (R_i - R_j)} \right)^3.$$

This definition leads to the results of Fig. 2 when $R_1 = R_2$. Since the system is isotropic, the mean Voronoi volume can be calculated as:

$$W = \langle \langle W_i^s \rangle_{\hat{s}} \rangle_i = \langle \langle W_i^s \rangle \rangle_{\hat{s}} = \langle W_i^s \rangle_i.$$

**Calculation of the mean Voronoi volume.**— Having calculated the Voronoi cell exactly in Eq. 11, we now proceed to develop a probability theory of volume fluctuations in the spirit of the quasiparticle approximation.
used in $\mathbf{5}$ to obtain the mean Voronoi volume. For a given ball $i$, the calculation of $W^i_*$ reduces to finding the ball $j^*$ that minimizes $l_{ij}(\hat{s})$. We call $j^*$ the Voronoi ball for the ball $i$. We consider $r = r_{ij^*}$, $\cos \theta = \hat{s} \cdot \hat{r}_{ij}$, and $c = 2l_{ij^*}$. We have $c = r^2 - (R_i - R_j)^2$. Therefore, we just need to compute the inverse cumulative distribution function, denoted $P_>(c)$, to find all the balls $j$ with $l_{ij} > \frac{c}{2}$, and thus not contributing to the Voronoi volume of the ball $i$. The average Voronoi volume is then given by the expression

$$W = \frac{\pi}{6}(c^3) = \frac{\pi}{6} \int_0^\infty c^3 \frac{dP_>(c)}{dc} dc = \frac{\pi}{2} \int_0^\infty c^2 P_>(c) dc. \quad (9)$$

We calculate the mean Voronoi volume for the balls of radius $R_1$ and $R_2$ separately and then average them. We denote $P_1^>(c)$ and $P_2^>(c)$ the inverse cumulative distributions respectively, and $W = x_1^2 \int_0^\infty c^2 P_1^>(c) dc + (1 - x_1^2) \int_0^\infty c^2 P_2^>(c) dc$, and therefore,

$$P_>(c) = xP_1^>(c) + (1 - x)P_2^>(c). \quad (10)$$

**Calculation of $P_>(c)$.**—There are three salient steps in the calculation of $P_>(c)$: (i) The separation of $P_>(c)$ following Eq. (10). (ii) The separation of each term $P_i^>(c)$, $i = 1, 2$, into two contributions: a term taking into account the contact spheres, $P_0^>(c)$, and a bulk term, $P_1^>(c)$. The contact term clearly depends on $z_{ij}$. The bulk term averages over all spatial correlations of non-contact particles and, without significant loss of accuracy as shown below, we assume that it only depends on the average value of $W$. In principle, it is possible to use a more realistic form for this term, but this would render the problem practically unsolvable. (iii) The separation of $P_1^>(c)$ and $P_2^>(c)$ into two terms $P_{ij}^>(c)$ and $P_{ij}^>(c)$, $j = 1, 2$, for each species.

An assumption of the theory (to be tested a posteriori with computer simulations) is that all of these terms are independent. Thus

$$P_>(c) = xP_{ij}^1(c)P_{ij}^2(c)P_{ij}^3(c)P_{ij}^4(c) + (1 - x)P_{ij}^1(c)P_{ij}^2(c)P_{ij}^3(c)P_{ij}^4(c). \quad (11)$$

Also, we work in the limit of large number of particles leading to Boltzmann-like exponential distributions for each $P_{ij}^>(c)$ and $P_{ij}^>(c)$. Four important quantities are then defined: (i) $V^i_>(c)$ and (ii) $S^i_>(c)$: the excluded volume and surface on the ball, respectively, where no center of a ball $j$ can be located for a given ball $i$ and for a given $c$. (iii) $\rho_j$: the average number of balls $j$ by the left free volume. (iv) $\rho^i_j$: the mean number of balls $j$ by the left free surface on a ball $i$. These considerations lead to:

$$P_{ij}^>(c) = \exp \left(- \rho_j V^i_>(c) \right), \quad (12)$$

$$P_{ij}^>(c) = \exp \left(- \rho^i_j S^i_>(c) \right).$$

Next, we calculate these four quantities. To simplify we denote $l = R_i + R_j$, $k = R_i - R_j$ and $\Theta$ the step-function. We obtain:

$$S^i_>(c) = \int \Theta(c - l^2 - k^2) \frac{ds}{dc} = 2\pi \int \Theta(c - l^2 - k^2) \frac{ds}{dc} = 2\pi \left(1 - \frac{l^2 - k^2 - kc}{lc} \right),$$

$$V^i_>(c) = \int \Theta(c - \frac{r^2 - k^2}{r \cos \theta - k}) dc^3 = 2\pi \frac{1}{4c}((c + k)^4 - l^4) + \frac{1}{3}(1 + k)^3 - l^3) + \frac{k^2}{x_2} + \frac{k_2}{x_2}((c + k)^2 - l^2),$$

$$\rho_j(W) = \frac{x_j}{W - \rho_j}. \quad (13)$$

where $x_1 = x$ and $x_2 = (1 - x)$. The fourth quantity, $\rho^i_j$, is the most difficult to calculate. In terms of the occupied areas Eqs. (2) we have $\rho^i_j = \frac{4\pi}{z_{ij}S_{occ}} - \frac{1}{z_{ij}S_{occ}}$. However, for the contact terms, the analogy with the Boltzmann-like exponential distribution of volumes is far from being exact. This is because this form is based on the large number limit which in the case of contacting balls is no more than around 6. Therefore, the exponential distribution is used as an Ansatz with $\rho^i_j$ a variational parameter as in $\mathbf{5}$. We denote $\langle S^i_{free} \rangle$ the mean solid angle of the gaps left between the $j$ contacting neighbors of a $i$ ball (Fig. 1a). We obtain:

$$\langle S^i_{free} \rangle = \int_0^\infty S^i_>(c) \frac{d(1 - P_>(c))}{dc} dc \approx \rho^i_j \int_0^{2\pi} S^i_>(c) \exp(-\rho^i_j S^i_>(c)) dc \approx \rho^i_j. \quad (14)$$

Then, we perform numerical simulations to find $\langle S^i_{free} \rangle$. We randomly generate balls of radius $R_i$ and $R_j$ with the proportion $z_1/\pi$ and $z_2/\pi$ respectively around a ball of radius $R_i$ and then evaluate the mean free surface $\langle S^i_{free} \rangle$ and its inverse to obtain $\rho^i_j$. We find

$$\rho^i_j(z_{ij}) = \frac{z_{ij}}{2\pi} \left(1 - \frac{z_{11} S_{occ}}{z_{11} \frac{2\pi}{z_1} - \frac{z_{12} S_{occ}}{z_{11} \frac{2\pi}{z_1}} \right) = \frac{z_{ij}}{2\pi} \left(1 - \frac{R_1}{R_i + R_1} \right)^2 \frac{z_{ij}}{z_1} \sqrt{1 - \left(\frac{R_2}{R_i + R_2} \right)^2}, \quad (15)$$

which is a generalization of the results of $\mathbf{5}$ to polycrystalline systems.

Using Eqs. (12), (13), and (15) into (11), $P_>(c)$ can be calculated by solving the equations numerically. Figure 2 depicts the comparison of the theoretical results of the probability of Voronoi volumes $P_>(c)$ with computer generated Hertzian packings with $z = 6$ for $x = 0.5$ at RCP. The calculated distribution is quite accurate for most of the range except for small deviations at high values of $c$, which however, do not affect much the value of the average $(c^3)$ in Eq. (10). This shows that our mean-field approximation already captures the main contribution of the probability distribution function $P_>(c)$. 


Calculation of $W$.— The above considerations lead to a final form to calculate $W$ using Eq. (11) into (9):

$$W = \frac{\pi}{2} \sum_i x_i \int_0^\infty c^2 \exp \left( \sum_j (-\rho_{ij} S_{ij}(c) - \rho_j(W) V_{ij}^*(c)) \right) dc.$$  

(16)

Notice that $\rho_j(W)$ depends on $W$, Eq. (13), and $\rho_{ij} z_{ij}$ depends on $z_{ij}$, Eq. (15), which in turn depends on the concentration $x$ and $z$ through Eq. (4). Therefore Eq. (16) is self-consistent to obtain $W(z,x)$, for a given $R_1/R_2$. A numerical integration of Eq. (16) is performed versus $x$ for a given value of $z$. By considering the isostatic limits of $z = 6$ and $z = 4$ we predict the limits of RCP and RLP at zero friction and infinite friction between the spheres, respectively. The results for the volume fraction at RCP versus $x$ are depicted in Fig. 4 which also compares the results to numerically generated packings of Hertz spheres [5]. We see a very good agreement indicating that the theory captures well the behavior of polydisperse packings and that the approximations used are reasonable. For size ratios larger than 2 deviations are found indicating the limit of validity of the approach. For any other value of interparticle friction between 0 and $\infty$, the density is obtained by setting $z$ between the limiting isostatic values of 6 and 4, respectively. The resulting volume fraction is shown in Fig. 3. The result for RLP for a given $x$ is a new prediction as this problem has not been investigated before. Our results promote new experiments to test the RLP limit of polydisperse systems shown in Fig. 3.

The formalism can be extended to consider any distribution of sphere radius. The main modification is that all the sums over the radius are replaced by integrations over the desired distribution of radius $P(R)$ (the binary case corresponds to two delta-functions at $R_1$ and $R_2$).

And all the quantities are calculated for balls of internal radius $r$ and external $R$ and $x$ and $(1-x)$ are replaced by $P(r)dr$ and $P(R) dR$, respectively, including the coordinates (see Supplementary Information B). This result allows to explore the space of radius distributions in search of the optimal packings for a given polydispersity. This analysis could be of industrial interest if one wishes to optimize the packing fraction by introducing different species in the mixture.

We calculate the volume fraction for several distributions $P(R)$ constraint by ball radius in the range $[1,2]$, in search of the optimal packing. We calculate the volume fraction for various $P(R)$ ranging from uniform to two-peak Gaussian distributions of varied widths. We find that the more small balls we add the better the packing until a certain point where the volume fraction starts to decrease. This maximum can be rationalized assuming that the small balls always fill the gaps between the large ones as long as there are enough large balls. Further extensions of the theory to any dimension can be performed by replacing 3 by $d$ in Eq. (7) and developing a theory of volume fluctuation in $d$-dimensions. We notice that many of the approximations employed in 3d may become exact for large $d$, thus we expect improved results in the mean field limit of infinite dimensions.

The method allows to treat more difficult problems. For instance, the prediction of the volume fraction of a jammed system of non-spherical particles is a longstanding problem. Theoretical predictions of Onsager [6] are valid for large aspect ratios, like elongated rods. Experiments however, find interesting new physics for small aspect ratios. In this respect, the present polydisperse theory could be mapped to the problem of ellipsoids, spherocylinders or rods. A Voronoi cell needs to be calculated as a function of the angles defining the orientation of the non-spherical particles in analogy of the calculation between two particles of different radii. The integration over $P(r)dr$ in Eq. (13) is then replaced by integration over weighted orientational angles. The above analysis could also be extended to dimensions beyond three. Although many of the approximations should work better in higher dimensions, some of the hypotheses (for example, the contact term ansatz) need to be reassessed. Thus, higher dimensions studies cannot be addressed as trivial extensions and need to be handled with care.

In summary, a theoretical framework is presented that predicts the RLP and RCP limits of a system of polydisperse spheres and brings together distinct results into a common theoretical framework. The formalism has the potential to solve other problems in condensed matter physics such as the mixing and phase behavior of systems of hard particles of different shapes and size.

FIG. 3: (a) Comparison between theory and numerical simulations of Hertzian packings at RCP, i.e. $z = 6$ versus $x$ for different values of $R_1/R_2$ as indicated. Error bars are std over 10 realizations of the packings with 10,000 balls. (b) Three dimensional surface plot of $\phi$ as a function of $z$ and $x$ for $R_1/R_2 = 1.5$. The numerical results at RCP and RLP are provided in Supplementary Information A.
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Appendix A: Table of volume fraction values predicted by the theory.

| $R_2/R_1$ | $x$  | 0  | 0.1 | 0.2 | 0.3 | 0.4 | 0.5 | 0.6 | 0.7 | 0.8 | 0.9 |
|-----------|------|----|-----|-----|-----|-----|-----|-----|-----|-----|-----|
| 1.3       | 0.5359 | 0.5376 | 0.5392 | 0.5403 | 0.5416 | 0.5423 | 0.5426 | 0.5423 | 0.5413 | 0.5393 |
| 1.5       | 0.5359 | 0.5393 | 0.5426 | 0.5456 | 0.5482 | 0.5503 | 0.5516 | 0.5517 | 0.5499 | 0.5453 |
| 1.7       | 0.5359 | 0.5409 | 0.5457 | 0.5506 | 0.5550 | 0.5588 | 0.5616 | 0.5628 | 0.5611 | 0.5399 |

TABLE I: Volume fraction for $z = 4$, RLP.

| $R_2/R_1$ | $x$  | 0  | 0.1 | 0.2 | 0.3 | 0.4 | 0.5 | 0.6 | 0.7 | 0.8 | 0.9 |
|-----------|------|----|-----|-----|-----|-----|-----|-----|-----|-----|-----|
| 1.3       | 0.6340 | 0.6356 | 0.6370 | 0.6382 | 0.6392 | 0.6399 | 0.6402 | 0.6399 | 0.6389 | 0.6340 |
| 1.5       | 0.6340 | 0.6372 | 0.6401 | 0.6423 | 0.6453 | 0.6472 | 0.6484 | 0.6484 | 0.6468 | 0.6426 |
| 1.7       | 0.6340 | 0.6386 | 0.6431 | 0.6475 | 0.6515 | 0.6549 | 0.6575 | 0.6586 | 0.6571 | 0.6506 |

TABLE II: Volume fraction for $z = 6$, RCP.

Appendix B: Distribution of sphere radius.

According to the theory, the average Voronoi volume for a packing with a distribution of radius $P(r)$, is given by the following self-consistent equation:

$$W = \frac{\pi}{2} \int dr P(r) \int_0^\infty c^2 \exp \left( \int dR(-\rho^2 R S^*_{rR}(c) - \rho R(W) V_{rR}(c)) \right) dc,$$

where the different quantities are calculated as follow:

$$S^*_{rR}(c) = \int \Theta(c - \frac{l^2 - k^2}{l \cos \theta - k}) ds = 2\pi (1 - \frac{l^2 - k^2 + kc}{lc}),$$

$$V^*_{rR}(c) = \int \Theta(c - \frac{r^2 - k^2}{r \cos \theta - k}) dr = 2\pi \left( -\frac{1}{4c}((c - k)^4 - l^4) + \frac{1}{3}(c - k)^3 - l^3 \right) + \left( \frac{k^2}{2c} - \frac{k}{2} \right)((c - k)^2 - l^2),$$

To simplify we denoted $l = r + R$, $k = r - R$ and $\Theta$ the step-function.

$$\rho_R(W) = \frac{P(R)}{W - V_g},$$

$$\rho^2_{rR} = \frac{z_{rR}}{2\pi} \int_0^\infty \frac{z_{rr'}}{z_r} \sqrt{1 - \left( \frac{r'}{r + r'} \right)^2} dr',$$

$$z_r = z \frac{A}{\lambda^*},$$

$$\langle S^*_{rR} \rangle = \int_0^\infty 2\pi (1 - \sqrt{1 - \left( \frac{r'}{r + r'} \right)^2}) P(r') dr',$$

$$A^{-1} = \int_0^{\infty} \frac{P(r')}{\langle S^*_{rR} \rangle} dr',$$

$$z_{rr'} = \frac{z_r z_{rr'} P(r')}{z}.$$