Packing fraction of trimodal spheres with small size ratio: An analytical expression

H. J. H. Brouwers

Department of the Built Environment, Eindhoven University of Technology, P.O. Box 513, 5600 MB Eindhoven, The Netherlands

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In previous papers analytical expressions were derived and validated for the packing fraction of bimodal hard spheres with small size ratio, applicable to ordered (crystalline) [H. J. H. Brouwers, Phys. Rev. E **76**, 041304 (2007); **78**, 011303 (2008)] and disordered (random) packings [H. J. H. Brouwers, Phys. Rev. E **87**, 032202 (2013)]. In the present paper the underlying statistical approach, based on counting the occurrences of uneven pairs, i.e., the fraction of contacts between unequal spheres, is applied to trimodal discretely sized spheres. The packing of such ternary packings can be described by the same type of closed-form equation as the bimodal case. This equation contains the mean volume of the spheres and of the elementary cluster formed by these spheres; for crystalline arrangements this corresponds to the unit cell volume. The obtained compact analytical expression is compared with empirical packing data concerning random close packing of spheres, taken from the literature, comprising ternary binomial and geometric packings; good agreement is obtained. The presented approach is generalized to ordered and disordered packings of multimodal mixes.

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I. INTRODUCTION

Models of ternary random packings were reported in [1–6], and experiments in [7,8]. In the present paper ternary sphere packings with small size ratio are studied, based on the approach as used for bimodal spheres [9]. In [9] analytical equations were derived for the packing of bimodal hard spheres with small size ratio, using a statistical approach by counting the fraction of uneven pairs. The derived packing fraction, applicable to ordered (crystalline) and disordered (random) arrangements, appeared to be in close agreement with computational and empirical hard sphere data from the literature. Here it is shown that the underlying approach, the volume distortion introduced by unequal sphere pairs, can be extended to assemblies consisting of three (and more) discretely sized spheres with small size ratio. The resulting packing expression, which does not contain any fitting parameter, is validated by an extensive comparison with published empirical ternary random close packing fractions, and found to be in good quantitative agreement.

II. PACKING FRACTION OF TRIMODAL SPHERE PACKINGS

In order to study the trimodal packing fraction of hard spheres, in this section the theory [9] on bimodal sphere packings with small size ratio is extended. For an arrangement of trimodal spheres, the mean sphere volume readily follows as

$$\Omega = X_1\Omega_1 + X_2\Omega_2 + X_3\Omega_3 = \frac{\pi\left(X_1 d_1^3 + X_2 d_2^3 + X_3 d_3^3\right)}{6}, \tag{1}$$

with X as the number fraction and the subscripts 1, 2, and 3 referring to the large, medium, and small spheres, respectively. Analogous to the bimodal arrangement, the average volume, using the statistically probable combinations of the three sphere sizes [9,10], follows as

$$V = \sum_{k=0}^{n}\sum_{i=0}^{n-k}\binom{n}{k}\binom{n-k}{i}X_1^{n-i-k}X_2^iX_3^k\left[\frac{n-i-k}{n}\ell_1^3 + \frac{i}{n}\ell_2^3 + \frac{k}{n}\ell_3^3 + \lambda_{12}\left(\ell_1^3-\ell_2^3\right) + \lambda_{13}\left(\ell_1^3-\ell_3^3\right) + \lambda_{23}\left(\ell_2^3-\ell_3^3\right)\right], \tag{2}$$

with n the number of spheres that form the elementary building block of the considered packing arrangement. By definition the characteristic volume V and length ℓ is related to the sphere diameter and monosized packing fraction f_1 as $\ell_i^3 = V_i = \frac{\pi}{6}d_i^3/f_1$ for $i = 1$, 2, or 3 [11]. The first terms appearing in the summation yield

$$\sum_{k=0}^{n}\sum_{i=0}^{n-k}\binom{n}{k}\binom{n-k}{i}X_1^{n-i-k}X_2^iX_3^k \times\left(\frac{n-i-k}{n}\ell_1^3 + \frac{i}{n}\ell_2^3 + \frac{k}{n}\ell_3^3\right) = X_1\ell_1^3 + X_2\ell_2^3 + X_3\ell_3^3, \tag{3}$$

which constitutes the expected value of the probability mass function of the trinomial distribution.

In Eq. (2) the lattice distortion is accounted for by the terms containing the factor λ_{ij}, which allows for the spacing resulting from the combination of the unequal spheres i and j; uneven pairs of spheres are considered as distorted contacts. This distortion is only found in the case where unequal spheres are present in a building block; for blocks that do not contain spheres of type i and/or j, it holds that $\lambda_{ij} = 0$.

As the size ratios of the three spheres are small, it can be assumed that the large scale structure of the system is not changed, and it is supposed that the volume distortion is a linear function of the volume mismatch. The distortion indeed tends to zero when ℓ_i^3/ℓ_j^3 tends toward unity, that is, when a monosized system is obtained and V should tend to Ω/f_1. For the bimodal packings ($X_3 = 0$ and hence

$\lambda_{13}=\lambda_{23}=0$), it was seen that the distortion parameter λ_{12} is proportional to the number of distorted contacts divided by the total number of contacts of the considered characteristic volume. A combinatorial computation of the possible bimodal configurations for ordered (crystalline) and disordered (random) arrangements showed that in general terms λ_{12} reads [9]

$$\lambda_{12}=C\frac{b_{12}(i)}{2b_t}=C\frac{\binom{n-2}{i-1}}{\binom{n}{i}}=C\frac{i\,(n-i)}{n\,(n-1)}\,(1\leqslant i\leqslant n-1)\,, \tag{4}$$

where C is a proportionality constant. Equation (4) is also applicable when the thermodynamic limit is taken, with i and n going to infinity and i/n = constant. This is a different interpretation to the case where n is taken to be a small constant which is the smallest identifiable cluster size or unit cell size in the case of ordered arrangements. So, it appears that the equations are valid not only for regular (crystalline) structures, but also for irregular (random) structures where the number of spheres may be infinite [9].

The bimodal insight can also be used in considering the trimodal system. The distortion between large spheres (d_1) on the one hand and the combined medium (d_2) and small (d_3) spheres is proportional to

$$\lambda_{1(2+3)}=C\frac{\binom{n-2}{i+k-1}}{\binom{n}{i+k}}=C\frac{(i+k)\,(n-i-k)}{n\,(n-1)}, \tag{5}$$

and likewise, between medium and the two other size groups; between small and the two other size groups it reads

$$\lambda_{2(1+3)}=C\frac{\binom{n-2}{i-1}}{\binom{n}{i}}=C\frac{i(n-i)}{n\,(n-1)},$$
$$\lambda_{3(1+2)}=C\frac{\binom{n-2}{k-1}}{\binom{n}{k}}=C\frac{k\,(n-k)}{n(n-1)}. \tag{6}$$

Since

$$\begin{aligned}\lambda_{12}+\lambda_{13}&=\lambda_{1(2+3)},\\ \lambda_{12}+\lambda_{23}&=\lambda_{2(1+3)},\\ \lambda_{13}+\lambda_{23}&=\lambda_{3(1+2)},\end{aligned} \tag{7}$$

there are three equations with three unknowns. Inserting Eqs. (5) and (6) and solving this set of linear equations yields

$$\begin{aligned}\lambda_{12}&=C\frac{i\,(n-i-k)}{n\,(n-1)},\\ \lambda_{23}&=C\frac{ik}{n\,(n-1)},\\ \lambda_{13}&=C\frac{k\,(n-i-k)}{n\,(n-1)}.\end{aligned} \tag{8}$$

These equations confirm that $\lambda_{12}=0$ when $i=0$, that is, when no medium sized spheres (d_2) are present. Also in the case of $i+k=n$ this λ_{12} distortion is not occurring, as then large spheres (d_1) are absent in the packing. Similar considerations hold for λ_{23} when $i=0$ and/or $k=0$, and for λ_{13} when $k=0$ and/or $i+k=n$; see Eq. (8). This is the reason that the summations of Eq. (2) need modified lower and upper bounds:

$$\begin{aligned}&\sum_{k=1}^{n}\sum_{i=1}^{n-k}\binom{n}{k}\binom{n-k}{i}X_1^{n-i-k}X_2^iX_3^k\left[\lambda_{12}\left(\ell_1^3-\ell_2^3\right)+\lambda_{13}\left(\ell_1^3-\ell_3^3\right)+\lambda_{23}\left(\ell_2^3-\ell_3^3\right)\right]\\ &=C\sum_{k=0}^{n-2}\sum_{i=1}^{n-k-1}X_1^{n-i-k}X_2^iX_3^k\left[\frac{(n-2)\,!}{(i-1)\,!k!\,(n-i-k-1)\,!}\right]\left(\ell_1^3-\ell_2^3\right)\\ &\quad+C\sum_{k=1}^{n-1}\sum_{i=0}^{n-k-1}X_1^{n-i-k}X_2^iX_3^k\left[\frac{(n-2)\,!}{i!\,(k-1)\,!\,(n-i-k-1)\,!}\right]\left(\ell_1^3-\ell_3^3\right)\\ &\quad+C\sum_{k=1}^{n-1}\sum_{i=1}^{n-k}X_1^{n-i-k}X_2^iX_3^k\left[\frac{(n-2)\,!}{(i-1)\,!\,(k-1)\,!\,(n-i-k)!}\right]\left(\ell_2^3-\ell_3^3\right)\\ &=CX_1X_2\left(\ell_1^3-\ell_2^3\right)+CX_1X_3\left(\ell_1^3-\ell_3^3\right)+CX_2X_3\left(\ell_2^3-\ell_3^3\right),\end{aligned} \tag{9}$$

as

$$\begin{aligned}\sum_{k=0}^{n-2}\sum_{i=1}^{n-k-1}X_1^{n-i-k}X_2^iX_3^k\left[\frac{(n-2)\,!}{(i-1)\,!k!\,(n-i-k-1)\,!}\right]&=X_1X_2\sum_{k=0}^{n-2}\sum_{i=1}^{n-k-1}X_1^{n-i-k-1}X_2^{i-1}X_3^k\left[\frac{(n-2)\,!}{(i-1)\,!k!\,(n-i-k-1)\,!}\right]\\ &=X_1X_2,\end{aligned} \tag{10}$$

and in view of $X_1 + X_2 + X_3 = 1$. Equation (10) applies, *mutatis mutandis*, also to the two other summation terms featuring in Eq. (9). Hence, Eq. (2), inserting Eqs. (3) and (9), becomes

$$V = X_1\ell_1^3 + X_2\ell_2^3 + X_3\ell_3^3 + CX_1X_2\left(\ell_1^3 - \ell_2^3\right) + CX_1X_3\left(\ell_1^3 - \ell_3^3\right) + CX_2X_3\left(\ell_2^3 - \ell_3^3\right). \quad (11)$$

Apparently, the distortion between i and j spheres can generally be accounted for by the terms X_iX_j, i.e., the product of the two number fractions. This expression is similar as for the bimodal system, where this term reads $X_1(1–X_1) = X_1X_2$ [9].

Introducing the size ratios,

$$u_{12} = \frac{\ell_1}{\ell_2} = \frac{d_1}{d_2}; \quad u_{23} = \frac{\ell_2}{\ell_3} = \frac{d_2}{d_3}, \quad (12)$$

using $X_3 = 1–X_1–X_2$, and inserting Eq. (1) yields as scaled trimodal packing fraction,

$$\frac{\kappa}{f_1} = \frac{\Omega}{f_1V} = \frac{X_1\left(u_{12}^3u_{23}^3 - 1\right) + X_2\left(u_{23}^3 - 1\right) + 1}{X_1\left(u_{12}^3u_{23}^3 - 1\right) + X_2\left(u_{23}^3 - 1\right) + 1 + CX_1X_2\left(u_{12}^3u_{23}^3 - u_{23}^3\right) + CX_1X_3\left(u_{12}^3u_{23}^3 - 1\right) + CX_2X_3\left(u_{23}^3 - 1\right)}. \quad (13)$$

To obtain this equation, Ω and V were divided by d_3 and ℓ_3, respectively. For u_{12} and u_{23} tending to unity this expression reduces to

$$\mathrm{K} = f_1\left[1 - CX_1X_2\left(u_{12}^3u_{23}^3 - u_{23}^3\right) + CX_1X_3\left(u_{12}^3u_{23}^3 - 1\right) + CX_2X_3\left(u_{23}^3 - 1\right)\right]. \quad (14)$$

The coefficient C, which is a nonadjustable parameter, depends on the type of packing, crystalline ($C = 1$) [10] or random ($C = -0.096$) [9]. For $C > 0$ the volume expands (compared to the mean sphere volume) and the packing fraction decreases, and for $C < 0$ the volume contracts. The aforementioned C values and the resulting effect on polydisperse packing reflect the different characteristics of crystalline and random packings. Here, this coefficient appears in the last three terms of Eq. (11); this distortion expression governs the volume distortion involved with three sphere sizes.

III. MODEL APPLICATION

In this section the derived packing expression, for small size ratio, is compared with empirical data concerning random close sphere packings. In the considered trimodal random sphere packings the subsequent sphere sizes have a constant ratio u, so

$$u_{12} = u_{23} = u. \quad (15)$$

The packing of such systems, with $u = 2$, was measured by [8] (see also [6] for the ternary diagram) concerning the combinations of 7-, 14-, and 28-mm steel spheres. Two types of distributions are considered here, viz., a binomial and a geometric. Also the bimodal packing consisting of small and large spheres only is addressed as reference.

A. Binomial distributions

For the binomial distribution of n sphere sizes and probability p, their number fractions for $i = 1, 2,\ldots, n$, are given as

$$X_i = \binom{n-1}{i-1} p^{n-i}(1-p)^{i-1}. \quad (16)$$

For the trimodal distribution holds $n = 3$ and $i = 1$, 2, and 3, and hence it follows that $X_1 = p^2$, $X_2 = 2p(1-p)$, and $X_3 = (1-p)^2$. Substituting these number fractions and Eq. (15) into Eq. (13) yields

$$\frac{\kappa}{f_1} = \frac{[p(u^3-1)+1]^2}{[p(u^3-1)+1]^2 + Cp(1-p)[2p^2(u^6-u^3) + p(1-p)(u^6-1) + 2(1-p)^2(u^3-1)]}. \quad (17)$$

For a number of p values the number fractions X_i are computed (Table I). The experimental void fractions presented in a ternary diagram [6,8] of steel ball packings are related to volume fractions. Accordingly, invoking that all spheres possess the same apparent density, the volume fractions are computed from the number fractions using

$$c_i = \frac{X_iu^{3(3-i)}}{X_1u^6 + X_2u^3 + X_3}, \quad (18)$$

for $i = 1$, 2, and 3, and the c_i are included in Table I as well, using $u = 2$. In the diagram [8] the pertaining measured trimodal void fraction j is read off, and included in Table I as well, together with the trimodal packing fraction κ ($= 1 - j$).

In Fig. 1, Eq. (17) is set out, using $C = -0.096$ [9] and $u = 2$. Also the empirical data from [6,8] as listed in Table I, scaled with $\varphi_1 = 0.364$ [8] and hence $f_1 = 0.636$, are included in this figure. One can see that upon combining three sphere sizes the maximum packing increase is 7%. For the bimodal binomial

TABLE I. Ternary void (j) and packing (κ) fractions as measured by Jeschar *et al*. [8] using discretely sized steel balls ($d_1 = 28$ mm, $d_2 = 14$ mm, and $d_3 = 7$ mm, i.e., $u_{12} = u_{23} = 2$) for compositions that follow a binomial number distribution with probability p.

p	X_1	X_2	X_3	c_1	c_2	c_3	j[a]	κ[a]
0	0	0	1	0	0	1	0.364	0.636
0.05	0.0025	0.095	0.9025	0.088	0.417	0.495	0.332	0.668
0.15	0.0225	0.255	0.7225	0.343	0.485	0.172	0.322	0.678
0.25	0.0625	0.375	0.5625	0.529	0.397	0.074	0.325	0.675
0.5	0.25	0.5	0.25	0.790	0.198	0.012	0.335	0.665
0.75	0.5625	0.375	0.0625	0.921	0.077	0.002	0.350	0.650
1	1	0	0	1	0	0	0.364	0.636

[a]Reference [8].

system, which is the most simple binomial distribution ($X_1 = p$ and $X_2 = 1 - p$), the maximum increase was about 5% [9]. Here again the agreement between ternary packing model and empirical data is good, though, for some of the computed packing fractions (between $p = 0.25$ and 0.75) the agreement would be better if p would be replaced by $p + 0.15$.

B. Geometric distributions

Next the packing of geometrically composed sphere mixes of n sizes is considered, i.e., the mixes that obey a power-law distribution for which it holds that [12]

$$c_i = \frac{c_i}{c_1 + c_2 + \cdots + c_{n-1} + c_n} = \frac{r^{n-i} c_n}{r^{n-1}c_n + r^{n-2}c_n + \cdots + rc_n + c_n} = \frac{r^{n-i}}{1 + r + r^2 + \cdots + r^{n-1}}, \tag{19}$$

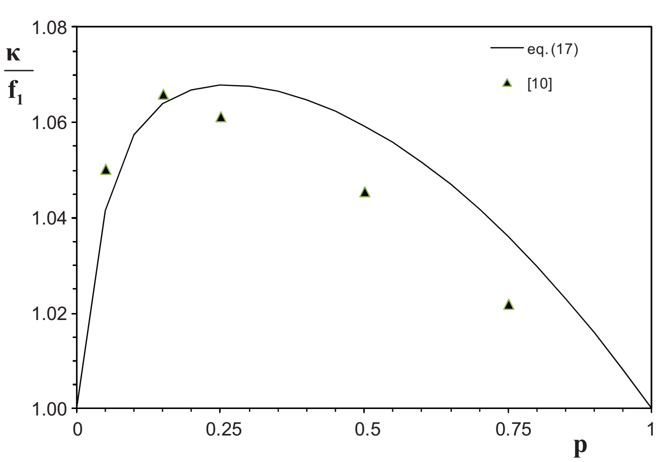

FIG. 1. (Color online) Random close packing fraction of binomially distributed trimodal spheres (size ratio $u = 2$), divided by the monosized packing fraction, as a function of the probability p. The graph contains Eq. (17) with $C = -0.096$, and measured values reported by [8], which are listed in Table I (and divided by the measured monosized packing value $f_1 = 0.636$).

and for spheres with the same apparent density the pertaining number fractions are

$$X_i = \frac{\frac{c_i}{d_i^3}}{\frac{c_1}{d_1^3} + \frac{c_2}{d_2^3} + \cdots + \frac{c_{n-1}}{d_{n-1}^3} + \frac{c_n}{d_n^3}} = \frac{\left(\frac{u^3}{r}\right)^{i-1}}{1 + \frac{u^3}{r} + \frac{u^6}{r^2} + \cdots + \left(\frac{u^3}{r}\right)^{n-2} + \left(\frac{u^3}{r}\right)^{n-1}}, \tag{20}$$

as

$$\frac{c_i}{c_{i+1}} = r; \quad \frac{d_i}{d_{i+1}} = u \tag{21}$$

[see also Eq. (15)], and hence

$$\frac{X_i}{X_{i+1}} = \frac{r}{u^3}. \tag{22}$$

Equation (22) reveals that the number distribution is also geometric; hence the spheres of subsequent size groups have the same volume (c) and number (X) ratios.

For $n = 3$ and $i = 1$, 2, and 3 the pertaining volume concentrations and number fractions are

$$c_i = \frac{\left(\frac{1}{r}\right)^{i-1}}{1 + \frac{1}{r} + \frac{1}{r^2}}; \quad X_i = \frac{\left(\frac{u^3}{r}\right)^{i-1}}{1 + \frac{u^3}{r} + \frac{u^6}{r^2}}. \tag{23}$$

Substituting the resulting X_1, X_2, and X_3 into Eq. (13), and using Eq. (15), yields

$$\frac{\kappa}{f_1} = \left[1 + C\frac{\left(\frac{u^6-u^3}{r^3} + \frac{u^6-1}{r^2} + \frac{u^3-1}{r}\right)}{\left(\frac{u^6}{r^2} + \frac{u^3}{r} + 1\right)\left(\frac{1}{r^2} + \frac{1}{r} + 1\right)}\right]^{-1} = \left[1 + CX_1c_1\left(\frac{u^6-u^3}{r^3} + \frac{u^6-1}{r^2} + \frac{u^3-1}{r}\right)\right]^{-1}; \tag{24}$$

see Eq. (23) for c_1 and X_1. In Fig. 2, Eq. (24) is set out versus α, defined as

$$\alpha = \log_u r, \tag{25}$$

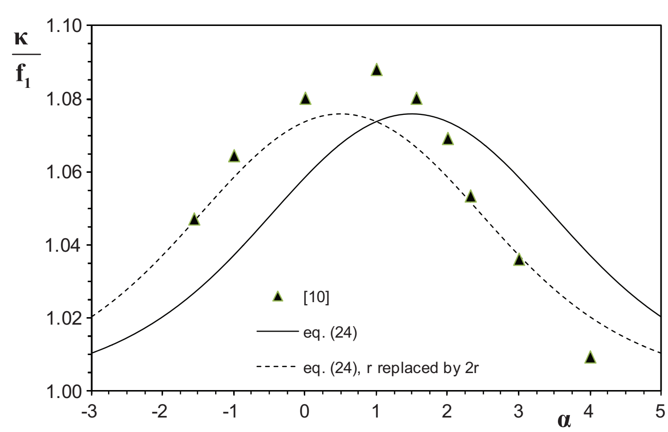

FIG. 2. (Color online) Random close packing fraction of geometrically distributed trimodal spheres (size ratio $u = 2$), divided by the monosized packing fraction, as a function of the power α. The graph contains Eq. (24) with $C = -0.096$, as well as Eq. (24) shifted by replacing r by $2r$, and measured values reported by [8], which are listed in Table II (and divided by the measured monosized packing value $f_1 = 0.636$).

TABLE II. Ternary void (j) and packing (κ) fractions as measured by Jeschar *et al.* [8] using discretely sized steel balls ($d_1 = 28$ mm, $d_2 = 14$ mm, and $d_3 = 7$ mm, i.e., $u_{12} = u_{23} = 2$) for compositions that follow a geometric volume distribution with power α, computed using Eq. (25).

α	r	c_1	c_2	c_3	j[a]	κ[a]
−1.58	1/3	0.077	0.231	0.692	0.334	0.666
−1	1/2	0.143	0.286	0.571	0.323	0.677
0	1	1/3	1/3	1/3	0.313	0.687
1	2	0.571	0.286	0.143	0.308	0.692
1.58	3	0.692	0.231	0.077	0.313	0.687
2	4	0.762	0.190	0.048	0.320	0.680
2.32	5	0.807	0.161	0.032	0.330	0.670
3	8	0.877	0.109	0.014	0.341	0.659
4	16	0.938	0.058	0.004	0.358	0.642

[a]Reference [8].

using $C = -0.096$ [9] and $u = 2$. The parameter α is the power appearing in the function F that governs the cumulative finer fraction of a geometric distribution [6,12]:

$$F(d_i) = \frac{d_i^\alpha - d_{n+1}^\alpha}{d_1^\alpha - d_{n+1}^\alpha} \ (\alpha \neq 0);$$
$$F(d_i) = \frac{\ln d_i - \ln d_{n+1}}{\ln d_1 - \ln d_{n+1}} \ (\alpha = 0). \tag{26}$$

For a number of r (and hence α) values, the pertaining c_i are included in Table II as well, using Eq. (23). In the ternary packing diagram the pertaining measured trimodal void fraction j is read off [6], [8], and included in Table II as well, together with the trimodal packing fraction κ ($= 1 - j$). A number of these measured values can also be found in [6]. The listed values of Table II, scaled using $\varphi_1 = 0.364$ [8] and hence $f_1 = 0.636$, are included in Fig. 2. This figure shows a good agreement between model and measured data. As some of the model predictions seem to be shifted from experimental data, another model line is shown whereby α is moved one unit to the left (implying a multiplication of r by 2). After this shift the agreement with some of the measured values is better, which implies that when in Eq. (24) r is replaced by $2r$, the accuracy of model prediction for these cases is increased. Probably coincidentally, this factor of 2 is identical to the size ratio of the subsequent size fractions (u). It noteworthy to point out that, though the shifting constitutes an improvement for some of the data, the original (nonshifted) predictions as such are in good agreement with the data as well.

C. Bimodal mixes with size ratio $u^2 = 4$

In the previous subsections packing of trimodal systems were presented, whereby $u_{12} = u_{23} = 2$. The agreement was good, but this not so obvious. The size ratio between the largest and smallest spheres, $u_{13} = u_{12}u_{23} = u^2 = 4$, is namely not close to unity, whereas the current model is based on the approximation $u - 1 \downarrow 0$. To explore the application limit of the presented model, the model is applied to the bimodal packing of largest and smallest spheres only, so by omitting the medium sized sphere (d_2), hence $c_2 = 0$. From Eq. (13) it follows that the scaled bimodal packing fraction, termed η/f_1 [9,10], reads

$$\frac{\eta}{f_1} = \frac{X_1(u_{12}^3u_{23}^3 - 1) + 1}{X_1(u_{12}^3u_{23}^3 - 1) + 1 + CX_1X_3(u_{12}^3u_{23}^3 - 1)} = \frac{X_1(u^6 - 1) + 1}{X_1(u^6 - 1) + 1 + CX_1X_3(u^6 - 1)}; \tag{27}$$

see Eq. (15). This equation is compared with the measured bimodal void and packing fraction of [8], the values can be found along one edge (compositional range from 7 to 28 mm) of their ternary diagram. In Fig. 3, their scaled bimodal packing values are included, as well as Eq. (27), whereby the number fraction is computed from the volume fraction by using

$$X_1 = \frac{\frac{c_1}{d_1^3}}{\frac{c_1}{d_1^3} + \frac{c_3}{d_3^3}} = \frac{c_1}{c_1(1 - u_{12}^3u_{23}^3) + u_{12}^3u_{23}^3} = \frac{c_1}{c_1(1 - u^6) + u^6}; \tag{28}$$

see Eqs. (12), (15), (21) and in view of $c_1 + c_3 = 1$.

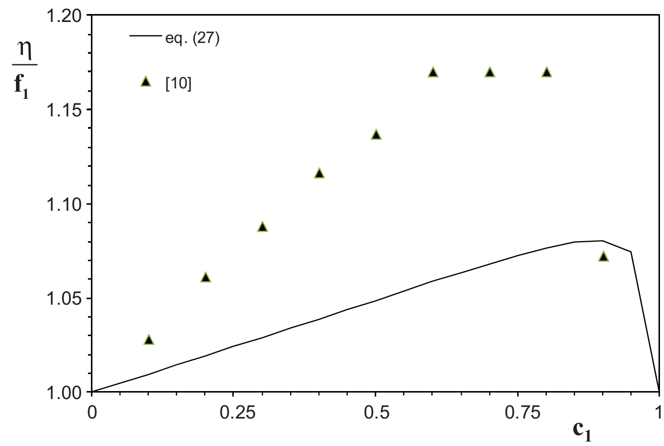

FIG. 3. (Color online) Random close packing fraction of bimodal mixes, divided by the monosized packing fraction, as a function of the large volume fraction c_1. The graph contains Eq. (27) with $C = -0.096$ and size ratio $u_{12}u_{23} = u^2 = 4$, and measured values reported by [8], divided by the measured monosized packing value $f_1 = 0.636$.

Figure 3 reveals that the current model is no longer able to predict the packing fraction of these bimodal mixes. The maximum measured packing increase is about 16%, which is about double the figure as measured for the trimodal binomial and geometric packings presented previously (Figs. 1 and 2). Here, in the bimodal case, the model underestimates the measured values by about 50% (Fig. 3). So, in the trimodal case the model is still able to predict the packing fraction, which can be contributed to the present medium sphere size (d_2) which "bridges" the small and large spheres. This enables the maximum size ratio (d_1/d_3) of 4 to be covered. On the other hand, the model cannot cover this size ratio anymore when a bimodal mixture is concerned.

The maximum size ratio of 4 studied here might be the reason that, though the model of the ternary binomial and geometric packings performed well, it is not as good as for the bimodal system with size ratio 2 [9], as the discussed deviations and shifts for some ternary compositions reveal.

But again it should be mentioned that also without these shifts the agreement between predictions and reported data is good, especially when it is realized that the model is entirely based on a theoretical analysis and no adjustable parameters are introduced. A comparison of the bimodal model with measured data concerning spheres with a smaller size ratio of 2 (consisting of mixes of 7- and 14-mm and of 14- and 28-mm spheres [8]), however, shows the best agreement [9].

IV. CONCLUDING REMARKS

The present paper reveals that the distortion involved with uneven pairs of spheres (with small diameter ratio u) in a multimodal mix is governed by the product of their number fractions [13]. Hence, the packing fraction of trimodal arrangements of randomly placed hard spheres is described with a similar model as for bimodal packings, presented in [9]. This bimodal packing model proved to be accurate up to $u = 2$.

Also the trimodal packing fraction, Eq. (9), is characterized by a closed-form equation containing the number concentration of the three components (actually two, X_1 and X_2), the two sphere diameter ratios u_{12} and u_{23}, the expansion coefficient C and the products X_1X_2, X_1X_3, and X_2X_3. The magnitude of C is known for both ordered (crystalline) and disordered (random) packings, viz., $C = 1$ and $C = -0.096$, respectively, for which assemblies the current model is thus applicable.

This expression of trimodal spheres, with small size ratio, is compared extensively with empirical random close packing information from the literature, whereby binomial and geometric mix compositions are considered. Good agreement is found for these arrangements for which $u_{12} = u_{23} = 2$, i.e., subsequent size groups have the same diameter ratio. It is noteworthy that model and used parameters are based on physical principles, and no adjustable parameter has been introduced anywhere to achieve the presented results. It also follows that the presented model is accurate when the medium size fraction is present in the mix. In the absence of this fraction, resulting in a bimodal discretely sized mix with a size ratio of 4, the model loses its validity. In other words, the presented approach is applicable to packed systems where the size ratio of largest and smallest may be large, as long as there are sufficient intermediate fractions present such that the size ratio of two subsequent size fractions is smaller than 2. As discussed previously, the distortion caused by size groups i and j is then governed by $CX_iX_j(\ell_j^3 - \ell_i^3)$, with $\ell_j > \ell_i$.

The multimodal mix packing model is not valid only for random packings, but also for ordered (crystalline) packings. It is therefore also possible to use the packing fraction expressions of ordered and disordered packings to determine which arrangement yields the highest packing fraction. As demonstrated for bimodal mixes [10], such a topological comparison will yield amorphization thresholds.

[1] C. C. Furnas, Department of Commerce, Bureau of Mines, Report of Investigation Serial No. 2894, 1928; Bull. U. S., Bur. Mines **307**, 74 (1929); Ind. Eng. Chem. **23**, 1052 (1931).

[2] A. R. Dexter and D. W. Tanner, Nature **230**, 177 (1971).

[3] J. A. Dodds, Nature **256**, 187 (1975); J. Dodds and H. Kuno, *ibid*. **266**, 614 (1977); J. A. Dodds, J. Coll. Interface Sci. **77**, 317 (1980).

[4] J. Zheng, P. F. Johnson, and J. S. Reed, J. Am. Ceram. Soc. **73**, 1392 (1990).

[5] T. Aste, Phys. Rev. E **53**, 2571 (1996).

[6] H. J. H. Brouwers, Phys. Rev. E **84**, 042301 (2011).

[7] R. K. McGeary, J. Am. Ceram. Soc. **44**, 513 (1961).

[8] R. Jeschar, W. Pötke, V. Petersen, and K. Polthier, in *Proceedings of the Symposium on Blast Furnace Aerodynamics, Wollongong, Australia, September 25–27, 1975*, edited by N. Standish (Illawara Branch of the Australasian Institute of Mining and Metallurgy, Carlton, Australia, 1975), pp. 136–147.

[9] H. J. H. Brouwers, Phys. Rev. E **87**, 032202 (2013).

[10] H. J. H. Brouwers, Phys. Rev. E **76**, 041304 (2007); **78**, 011303 (2008).

[11] For crystalline packings the unit cell volume V_{cell} is obtained by multiplying V with N, the spheres' volume present in the unit cell. For example, $N = 1$, 2, and 4 for the sc, bcc, and fcc structures, respectively.

[12] H. J. H. Brouwers, Phys. Rev. E **74**, 031309 (2006); **74**, 069901(E) (2006); **84**, 059905(E) (2011).

[13] For multiple sphere sizes the line of reasoning as introduced here for trimodal mixes can be continued. Consider, for example, an assembly of three sphere sizes, to which a fourth size d_4 is added. The fraction of uneven contacts between the d_1 spheres on the one hand and d_2, d_3, and d_4 on the other, is proportional to $X_1(X_2 + X_3 + X_4)$. As the fraction of distorted contacts between d_1 and d_2 spheres and d_1 and d_3 spheres is proportional to X_1X_2 and X_1X_3, respectively, it readily follows that the fraction of distorted contacts between d_1 and d_4 spheres is proportional to X_1X_4. In other words, the term X_iX_j is applicable to any number and type of uneven sphere sizes that are combined. It is also worthwhile to point out that this principle is applicable to disordered and ordered arrangements.