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Random packing fraction of bimodal spheres: An analytical expression

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In previous papers analytical equations were derived and validated for the packing fraction of crystalline structures consisting of bimodal randomly placed hard spheres [Phys. Rev. E **76**, 041304 (2007); **78**, 011303 (2008)]. In this article it will be demonstrated that the bimodal random packing fraction of spheres with small size ratio can be described by the same type of closed-form equation. This equation contains the volume of the spheres and of the elementary cluster formed by these spheres. The obtained compact analytical expression appears to be in good agreement with a large collection of empirical and computer-generated packing data, taken from literature. By following a statistical approach of the number of uneven pairs in a binary packing, and the associated packing reduction (compared to the monosized limit), the number fraction of hypostatic spheres is estimated to be 0.548.

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I. INTRODUCTION

The random packing of spheres is an old physical puzzle and has received much attention the past few years (see, e.g., Refs. [1,2]). Attention has been paid to revealing packing geometries and the route to understanding liquids and amorphous materials and glasses. Countless numerical and experimental studies have confirmed a common lower limit for the random close packing (RCP) value of disordered frictionless sphere packings, f_1, having a consistent value of about 0.64 in three dimensions [3–17]. This reproducible value indicates that RCP corresponds to a well-defined "geometrical structure," yielding the perception that RCP of spheres should have a common structure. Mathematically, the RCP state is difficult to define because by introducing order, higher packing factions can be obtained. In Ref. [18] the "maximum random jammed" (MRJ) state was defined by configurations with minimal values of typical order parameters. Several studies have been executed with the aim to reveal a repeating geometric structure of RCP, often assemblies of face-adjacent tetrahedra ("polytetrahedra") that result in quasicrystal structures [19–21]. Also in (metallic) glasses and colloidal suspensions, which resemble hard sphere packings, local ordering was observed [22–31].

In the present paper binary random sphere packings with small size ratio are studied, following the same approach as in Refs. [1,2]. This study also reveals statistical information concerning the structure of randomly packed monosized spheres, in particular the fraction of hypostatic spheres in a random arrangement, and the minimum number of spheres involved in a cluster (or building block) of randomly packed spheres.

In Refs. [1,2] analytical equations were derived for the packing fraction of crystalline structures consisting of bimodal randomly placed hard spheres with small size ratio ($d_L/d_S = u$). The bimodal packing fraction was derived for the three crystalline cubic systems using a statistical approach of the uneven pairs. The derived lattice parameters of the bimodal unit cell appeared to be in close agreement with empirical hard sphere data from literature. To derive these equations, the number of involved spheres in the unit cell of the considered crystalline structure was relevant. It is shown that the underlying approach for studying the volume distortion introduced by unequal spheres pairs is also applicable to asymmetric and nonregular sphere assemblies, as is the case in randomly packed spheres. Furthermore, it is shown that the obtained expression for the bimodal packing fraction of the hard sphere lattices is very similar to the one of bimodal random close packings [32,33], which as such asserts the conjecture that they also possess a typical repeatable structure. Though, in the limit of $u \downarrow 1$, the bimodal packing fractions of both crystalline and random packings are both parabolic functions of the large (or small) sphere concentrations (c_L and c_S, respectively, $c_L + c_S = 1$), a crystalline packing fraction decreases and a random packing fraction increases upon combining two sphere sizes. Based on these insights, and building on the success of the original crystalline packing fraction function, an analytical expression for the RCP fraction of spheres is put forward, which is entirely governed by physically defined parameters (such as the monosized packing fraction value and the size ratio). This expression, which does not contain any fitting parameter, is validated by an extensive comparison with published empirical and computer-generated packing fractions, and found to be in good quantitative agreement. Subsequently, the model is applied to bimodal random loose packing (RLP) and generalized to all states of random packing.

Finally, the combinatorial approach to derive the packing fraction of binary crystalline structures, and here applied successfully to derive the RCP fraction of these spheres, is employed to study the nature of RCP of monosized spheres. Using the known bimodal packing increase, caused by volume contraction, the number fraction of hypostatic spheres involved in random packings (from RLP to RCP) is assessed.

II. BIMODAL CRYSTALLINE SPHERE PACKINGS

In order to study the bimodal RCP fraction of spheres, in this section the theory on crystalline structures consisting of bimodal randomly placed hard spheres, with small size ratio ($d_L/d_S = u$), is recapitulated and further elaborated. As a first step, the stacking of equal spheres in a lattice structure is addressed. The packing fraction follows from the number of spheres N with diameter d in the unit cell, the sphere volume

Ω, and the unit cell volume V_{cell}:

$$\mathrm{f}_1^{cp} = \frac{N\Omega}{V_{\text{cell}}} = \frac{N\frac{\pi}{6}d^3}{\ell^3}, \tag{1}$$

with ℓ as lattice constant or lattice parameter [1,2]. For example, for the fcc structure holds $N = 4$ and $\ell = 2^{1/2}d$, for the bcc structure $N = 2$ and $\ell = 2d/3^{1/2}$, and for the sc structure holds $N = 1$ and $\ell = d$, yielding as monosized packing fractions $f_1^{\text{fcc}} = 2^{1/2}\pi/6$, $f_1^{\text{bcc}} = 3^{1/2}\pi/8$, and $f_1^{\text{sc}} = \pi/6$, respectively.

For an arrangement of bimodal spheres, the mean sphere volume readily follows as

$$\begin{aligned}\Omega &= X_L\Omega_L + X_S\Omega_S = X_L\Omega_L + (1 - X_L)\Omega_S\\ &= \frac{\pi\left[X_L d_L^3 + (1 - X_L)d_S^3\right]}{6},\end{aligned} \tag{2}$$

with X as the number fraction and the subscripts S and L referring to small and large spheres, respectively. The cell volume, using the statistically probable combinations of small and large spheres [1,2], followed as

$$\begin{aligned}\mathrm{V}_{\text{cell}} = \sum_{i=0}^{n}\Bigg\{&\binom{n}{i}\, X_L^{n-i}(1 - X_L)^i\\ &\times\left[\frac{n-i}{n}\ell_L^3 + \frac{i}{n}\ell_S^3 + \lambda_i\left(\ell_L^3 - \ell_S^3\right)\right]\Bigg\},\end{aligned} \tag{3}$$

with n the number of spheres that form the elementary building block of the crystal structure considered. In Eq. (3), the lattice distortion is accounted for by the factor λ_i, which allows for the spacing resulting from the combination of the large and small spheres in the cells in which they both appear $(1 \leqslant i \leqslant n - 1)$. Their size ratio u is small, so that it can be assumed that the large-scale structure of the system is not changed as u varies, and it is supposed that the volume distortion is a linear function of the volume mismatch. The distortion indeed tends to zero when ℓ_S^3 tends to ℓ_L^3, that is, when a monosized system is obtained and V_{cell} should tend to $\ell_S^3 = \ell_L^3$. The distortion parameter λ_i is furthermore proportional to the number of distorted contacts (b_{LS}) divided by the total number of contacts (b_t) of the unit cell [2]. Uneven pairs of spheres are considered as distorted contacts. A combinatorial computation of the possible bimodal configurations for the fcc, bcc, and sc lattices showed that in general terms λ_{i} reads

$$\begin{aligned}\lambda_i &= C\frac{b_{LS}(i)}{2b_t} = C\frac{\binom{n-2}{i-1}}{\binom{n}{i}}\\ &= C\frac{i(n-i)}{n(n-1)} \quad (1 \leqslant i \leqslant n - 1),\end{aligned} \tag{4}$$

where C is a proportionality constant, which value follows from a boundary condition (as seen below). The natural question is whether Eq. (4) holds for every unit cell consisting of two types of spheres and sphere pairs. This question is answered affirmatively by a rigorous mathematical proof based on basal combinatorial and probabilistic counting arguments [34,35], which is recapitulated here.

Assume we have a contact network involving n spheres, of which i spheres are small. Choose one arbitrary contact involving spheres (really, vertices in a network) u and v. The total number of choices of spheres for u and v is $n(n - 1)$ by inspection, whereas for a distorted contact we can choose either u to be small (i choices) and v to be large ($n - i$ choices), or vice versa, resulting in $2i(n - i)$ possibilities. This gives us $b_{LS}(i)/b_t = 2i(n - i)/[n(n - 1)]$, independent of the choice for u and v, and yielding Eq. (4).

Surprisingly, this proof shows that the distortion depends only on the number of spheres and pairs of the sphere cluster, but not on the way the contacts are distributed among the spheres in this cluster. To summarize, by counting the possible uneven pairs to b_{LS} in an alternative way [34,35] it is affirmed that Eq. (4) is actually a generic formula for all clusters (and unit cells) that consist of two types of spheres. Inserting Eq. (4) in Eq. (3) yields

$$V_{\text{cell}} = X_L\ell_L^3 + (1 - X_L)\ell_S^3 + CX_L(1 - X_L)\left(\ell_L^3 - \ell_S^3\right). \tag{5}$$

Equation (5) 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 Refs. [1,2] the smallest building block of sc, bcc, and fcc lattices were identified, in order to be able to analyze all possible configurations, their probabilities, and their contribution to the distortion. The disadvantage of this approach was that it involved a lot of computations and that one needs to do a separate careful analysis for every different building block. From the generic solution presented here, this limitation is not needed anymore, so sphere arrangements comprising multiples of n and N would yield the same conclusion and equations [Eqs. (4) and (5)]. Furthermore, it appears that both equations are valid not only for regular (crystalline) structures as examined in Refs. [1,2], but also for irregular (random) structures where the number of spheres may be infinite, a feature that later will be utilized in examining RCP.

The two first terms on the right-hand side of Eq. (5) correspond to the so-called Retger's equation [1,2,36,37]. Combining the bimodal sphere volume, Eq. (2), with the bimodal cell volume, Eq. (5), and using the size ratio

$$u = \frac{\ell_L}{\ell_S} = \frac{d_L}{d_S}, \tag{6}$$

yields one general expression that governs the ratio of bimodal packing fraction η and unimodal packing fraction f_1:

$$\frac{\eta^{cp}}{f_1^{cp}} = \frac{X_L(u^3 - 1) + 1}{X_L(u^3 - 1) + 1 + C(1 - X_L)X_L(u^3 - 1)}, \tag{7}$$

where the superscript cp refers to crystalline packing. The numerator in this equation constitutes the mean sphere volume and the denominator the mean volume of the packing, both dimensionless.

In Refs. [1,2,38,39], it is assumed that upon the introduction of small spheres in a crystalline structure of large spheres only, it will not change the cell volume, in other words, each small sphere will be able to rattle in the cage formed by the substituted larger sphere. Mathematically, this implies that the first derivative of the cell volume with respect to X_L at

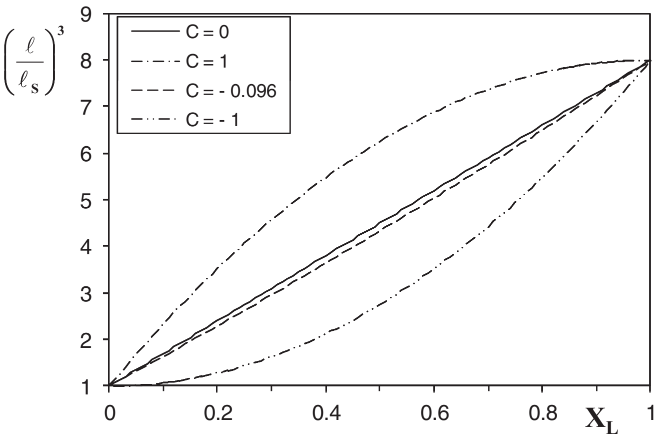

FIG. 1. Scaled mean packing volume $[(\ell/\ell_S)^3]$ following Eq. (5), for $C = -1$, -0.096, 0, and 1 versus the number fraction of large spheres in a bimodal mix. The line pertaining to $C = 1$ corresponds to the cell volume of crystalline sphere packings [1,2], $C = 0$ to Retger's equation [1,2,36,37], $C = -0.096$ to RCP and RLP of spheres, and $C = -1$ to a sphere arrangement where all spheres can be enlarged without volume expansion.

the large sphere side ($X_L = 1$) equals zero, that is to say,

$$\left.\frac{dV_{\text{cell}}}{dX_L}\right|_{X_L=1} = 0. \tag{8}$$

Applying this boundary condition to Eq. (5) yields $C = 1$. In Ref. [2] Eq. (5) with $C = 1$ was compared with empirical lattice space data [40], and good agreement was seen.

In Fig. 1, $\text{V}_{\text{cell}}/\ell_S^3$ is set out versus X_L for $u = 2$ and $C = 0$ (Retger's equation) and for $C = 1$. Retger's equation reflects that the cell volume is linearly proportional to the volume of the spheres it is containing, and hence the bimodal packing fraction equals the monosized packing fraction in the entire concentration range [see Eq. (7)]. For $C = 1$, Fig. 1 shows that the cell volume is larger than the Retger's equation, reflecting the expansion of the unit cell, yielding a reduced packing fraction (compared to the monosized value).

Furthermore, Eq. (7) yields as gradient $\beta^{cp} = -3/4(1 - \text{f}_1^{cp})$ for all crystalline structures [2], for β is defined by Refs. [32,33]

$$\beta = \frac{1}{f_1(1-f_1)}\left.\frac{d\eta}{du}\right|_{u=1,X_L=0.5} = \frac{-3C}{4(1-f_1)}. \tag{9}$$

In packing studies often the volume faction c is used (instead of the number fraction X). Expressed in the volume fraction of large constituent, c_L, using

$$\text{X}_L = \frac{c_L d_S^3}{c_S d_L^3 + c_L d_S^3} = \frac{c_L}{(1-c_L)u^3 + c_L}, \tag{10}$$

Eq. (7) reads

$$\frac{\eta^{cp}}{f_1^{cp}} = \frac{c_L(1-u^3)+u^3}{c_L(1-u^3)+u^3+C(1-c_L)c_L(u^3-1)}. \tag{11}$$

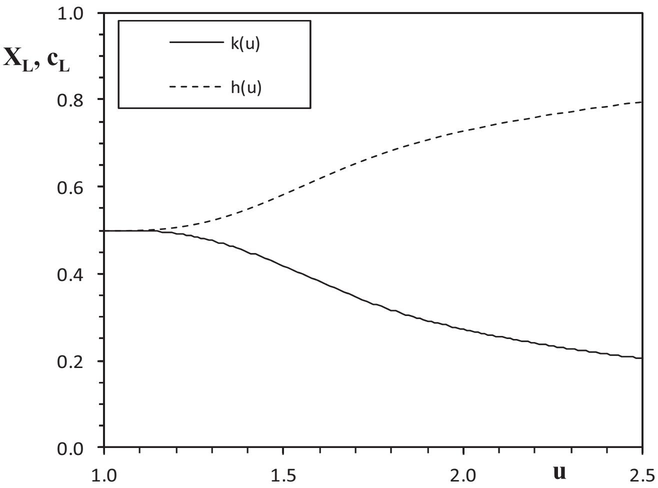

FIG. 2. Volume $[c_L = h(u)]$ and number $[X_L = k(u)]$ fraction of large spheres as a function of the size ratio (u) at minimum/maximum packing fraction for bimodal particle mixes with small size ratio (u).

The values of c_L at which the packing fraction (and void fraction) for a given size ratio has an extremum is denoted as $c_L = h(u)$ [32]. From the Appendix it follows as

$$\frac{dh}{du} = \left.\frac{\eta_{c_L}^{cp}}{\eta_u^{cp}}\right|_{c_L=h} = \frac{(u^3-1)[(h-1)^2u^3-h^2]}{3u^2(1-h)h}. \tag{12}$$

For $u \rightarrow 1$, $h(u)$ tends to $1/2$ and for $u > 1$, $h(u)$ follows from integrating Eq. (12), the result depicted in Fig. 2. Equation (12) reveals that the composition at which the packing fraction has an extremum does not depend on the factor C. Only the magnitude of the bimodal packing fraction depends on C. Obviously, this η^{cp} is also linearly proportional to the monosized packing fraction, as reflected in Eqs. (7) and (11). For $C > 0$, the packing fraction is reduced upon mixing and the extremum is a minimum, for $C < 0$ the void fraction is reduced and the extremum constitutes a maximum. The contraction and expansion of the cell volume is more pronounced the more C deviates from zero.

Also the number fraction X_L at which the packing fraction attains an extremum, denoted as $k(u)$ [1], can be computed similarly using the partial derivatives of Eq. (7). It readily follows (Appendix) that

$$k(u) + h(u) = 1. \tag{13}$$

In Fig. 2, $k(u)$ is included as well. Obviously, in view of Eq. (13), the curves $k(u)$ and $h(u)$ are symmetrical with respect to the line $c_L = X_L = 0.5$.

III. BIMODAL RANDOM SPHERE PACKINGS

In the present section the analysis of the previous section is extended to random sphere packings. From Eqs. (7) and (11) it follows that for $u \downarrow 1$ the bimodal packing fraction of crystalline arrangements can be asymptotically approximated by

$$\begin{aligned}\eta^{cp}(u,c_L) &= f_1^{cp} - 3f_1^{cp}C(1-X_L)X_L(u-1)\\ &= f_1^{cp} - 3f_1^{cp}C(1-c_L)c_L(u-1).\end{aligned} \tag{14}$$

Equation (14) illustrates that the packing fraction reduction is linearly proportional to the monosized packing fraction, the coefficient C and the size ratio u. It also asserts that for $u \downarrow 1$, $c \to X$, i.e., volume fraction and number coincide, which also follows from Eq. (10). The bimodal packing fraction of randomly packed particles with small size ratio u features the same characteristics, and reads [1,2]

$$\begin{aligned}\eta^{rp}(u,c_L) &= f_1^{rp} + 4\beta^{rp} f_1^{rp}\left(1-f_1^{rp}\right)(1-c_L)c_L\,(u-1)\\ &= f_1^{rp} + 4\beta^{rp} f_1^{rp}\left(1-f_1^{rp}\right)(1-X_L)X_L\,(u-1),\end{aligned} \tag{15}$$

where the superscript rp stands for random packing. Equations (14) and (15) readily reveal that near $u = 1$ the packing extremum is obtained when the two sphere concentrations are in parity, i.e. $X_L = c_L = 0.5$, as can be seen in Fig. 2.

In Refs. [1,2] the bimodal amorphous [Eq. (15) with $f_1^{\mathrm{rcp}} = 0.64$ and $\beta^{\mathrm{rcp}} = 0.20$] and crystalline fcc and bcc packing fractions [Eq. (7) with $C = 1$] were equated, yielding the optimum packing configuration, which depends on mixture composition and diameter ratio only. Maps of the closest packing mode were established and applied to colloidal mixtures of polydisperse spheres and to binary alloys of bcc, fcc, and hcp metals. The extensive comparison between the analytical expression and the published numerical and empirical data yielded good agreement.

It has been conjectured by many researchers that random packings also have a characteristic structure, since a reproducible packing fraction is found for a defined state of packing, such as random loose and random close packings (RLP and RCP, respectively) of spheres. As Eqs. (14) and (15) are very similar, and following Refs. [34,35] that the underlying statistics of the bimodal cluster volume is also applicable to irregular packings, it is intuitively proposed that the packing fraction of bimodal random packing, Eq. (15), is the asymptotic approximation for small u of

$$\begin{aligned}\frac{\eta^{rp}}{f_1^{rp}} &= \frac{c_L(1-u^3)+u^3}{c_L(1-u^3)+u^3-\frac{4}{3}\beta^{rp}\left(1-f_1^{rp}\right)(1-c_L)c_L(u^3-1)}\\ &= \frac{X_L(u^3-1)+1}{X_L(u^3-1)+1-\frac{4}{3}\beta^{rp}\left(1-f_1^{rp}\right)(1-X_L)X_L(u^3-1)},\end{aligned} \tag{16}$$

with $C = -\frac{4}{3}\beta^{rp}(1-f_1^{rp})$ inserted. Equation (16) represents a simple expression for the bimodal packing fraction, depending only on the packing mode of the mix (loose, dense, etc.), the composition, and the size ratio of the two spheres. For random close packed spheres, Eq. (16), using $f_1^{\mathrm{rcp}} = 0.64$ and $\beta^{\mathrm{rcp}} = 0.20$, is set out in Fig. 3(a).

In this figure also empirical data [4,6] and computer-generated data [5,7,13,41–44] concerning bimodal packings of spheres are included. The data from Ref. [41] is generated with the same model as referred to in Refs. [10,11], [42] data with the model in Refs. [12], [43] with Refs. [14,17], and Ref. [44] with Ref. [15]. The referred sources report different monosized RCP fraction values (f_1^{rcp}), viz., 0.634 (experiments [4], also referred to in Ref. [33]), 0.641 (simulations [5]), 0.625 (experiments [6]), 0.628 (simulations [7]), 0.6435 (simulations [13]), 0.637 (simulations [41]), 0.644 (simulations [42]), 0.637 (simulations [43]), and 0.634 (simulations [44]). Their bimodal packing values, set out in Fig. 3(a), are therefore all divided (scaled) by their monosized packing value.

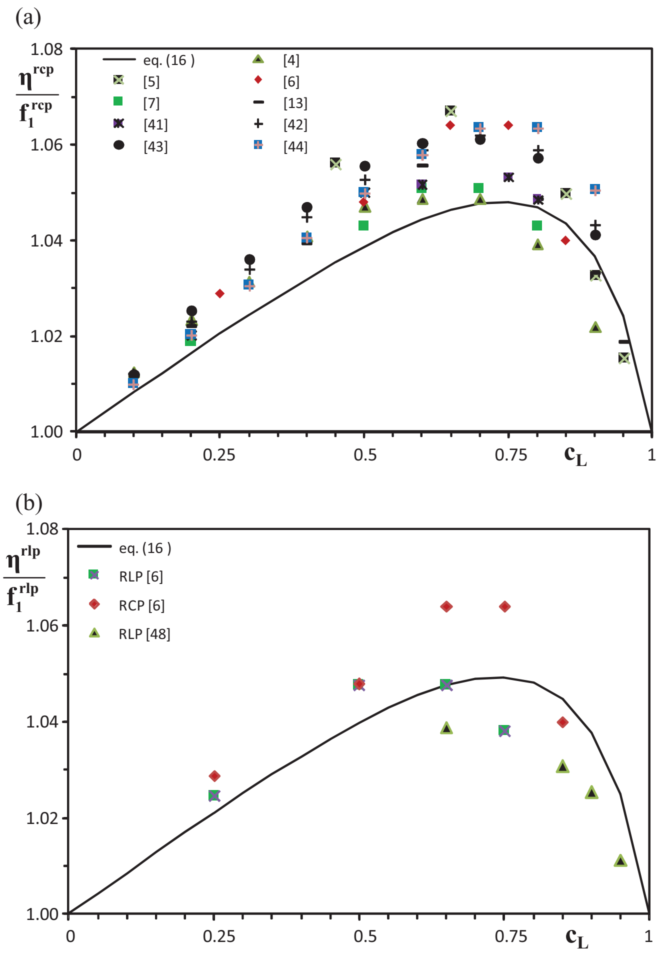

FIG. 3. (Color online) (a) Random close packing fraction of bimodal spheres (size ratio $u = 2$), divided by the monosized packing fraction, as a function of the large sphere volume fraction. The graph contains Eq. (16) with $f_1^{\mathrm{rcp}} = 0.64$ and $\beta^{\mathrm{rcp}} = 0.20$ [$\beta^{\mathrm{rcp}}(1 - \mathrm{f}_1^{\mathrm{rcp}}) = 0.072$], and empirical and computer-generated data from literature. These sources reported different monosized packing values (f_1^{rcp}), viz., 0.634 (experiments [4], also referred to in Ref. [33]), 0.641 (simulations [5]), 0.625 (experiments [6]), 0.628 (simulations [7]), 0.6435 (simulations [13]), 0.637 (simulations [41]), 0.644 (simulations [42]), 0.637 (simulations [43]), and 0.634 (simulations [44]). Their bimodal packing values are therefore all divided (scaled) by their monosized packing value. (b) Random loose packing fraction of bimodal spheres (size ratio $u = 2$), divided by the monosized packing fraction, as a function of the large sphere volume fraction. The graph contains Eq. (16) with $\mathrm{f}_1^{\mathrm{rlp}} = 0.54$ and $\beta^{\mathrm{rlp}} = 0.16$ [$\beta^{\mathrm{rlp}}(1 - \mathrm{f}_1^{\mathrm{rlp}}) \approx \beta^{\mathrm{rcp}}(1 - \mathrm{f}_1^{\mathrm{rcp}}) = 0.072$], empirical data [6], simulation data [48], all divided (scaled) by their monosized packing value (0.525 [6] and 0.577 [48]). Also the scaled RCP data from Ref. [6], taken from (a), are included.

Figure 3(a) confirms that all scaled bimodal RCP fractions are all matched remarkably well by a relatively simple analytical expression [Eq. (16)]. Generally, the analytical expression underestimates the computational and experimental values, which might be caused by that the expression is asymptotically correct when $u \downarrow 1$, where as the depicted packing fractions pertain to $u = 2$. What is particularly remarkable is that the present model is solely based on an analytical analysis, without introducing a fitting parameter. Both relevant parameters, the monosized packing fraction, f_1, and the monosized/bimodal packing fraction gradient, β, are namely physically defined and are functions only of the considered particle shape (here spheres) and the mode of packing (e.g., loose, close) [32,33]. Furthermore, one can see that the model also captures for which composition the maximum bimodal packing is attained when $u = 2$, viz.,$c_L \approx 0.66$, which can also be seen in Fig. 2. The previous section demonstrated that the composition at maximum packing fraction does not depend on the factor $\beta(1 - f_1)$ or C, so Fig. 2 also holds for the random packing considered here. According to the listed references and the current model, this packing increase is for RCP of spheres about 6% compared to the monosized situation [Fig. 3(a)].

In Fig. 1 the mean volume of a bimodal random close sphere packing is included by setting out Eq. (5) with $C = -\frac{4}{3}\beta^{\mathrm{rcp}}(1 - f_1^{\mathrm{rcp}})$ [see Eq. (9)] and substituting $f_1^{\mathrm{rcp}} = 0.64$ and $\beta^{\mathrm{rcp}} = 0.20$, yielding $C = -0.096$. One can see that this equation follows Retger's equation ($C = 0$) quite close (as $|C| \ll 1$), and that the volume is slightly smaller for $0 < X_L < 1$ as $C < 0$. In other words, for random mixtures the volume contracts (compared to the mean spheres volume Ω) and hence, the packing fraction is higher than the monosized value.

The presented approach can also be applied to random loose packing (RLP) of monosized spheres, for which also a reproducible packing fraction is found [3,6,16,45–49], with $f_1^{\mathrm{rlp}} \approx 0.54$ as a generally accepted value for this lower limit of random sphere packings. However, the β of RLP is not known, and here its magnitude is assessed by applying Eq. (16) to available bimodal packing information, which is scarce; only in Refs. [6] and [48] are experimental and computational data, respectively, presented. Their f_1^{rlp} amounts 0.525 [6] and 0.577 [48], and the scaled bimodal packing fraction is presented in Fig. 3(b). In this figure also the scaled RCP fractions as measured by Ref. [6] are included [taken from Fig. 3(a)].

From Fig. 3(b) one can conclude indeed that the measured (and scaled) RLP and RCP fractions are quite close to each other in the entire concentration range, especially for $c_L = 0.25$ and 0.5. This indicates that

$$\beta^{\mathrm{rlp}}\left(1 - f_1^{\mathrm{rlp}}\right) = \beta^{\mathrm{rcp}}\left(1 - f_1^{\mathrm{rcp}}\right). \tag{17}$$

Substituting $f_1^{\mathrm{rlp}} = 0.54$, $f_1^{\mathrm{rcp}} = 0.64$, and $\beta^{\mathrm{rcp}} = 0.20$ yields $\beta^{\mathrm{rlp}} = 0.16$, and Eq. (16) with these $\mathrm{f}_1^{\mathrm{rlp}}$ and β^{rlp} is drawn in Fig. 3(b). The lines drawn in Figs. 3(a) and 3(b) [Eq. (16)] are almost identical, and the agreement with the empirical RLP data from Refs. [6] and [48] is good. It thus appears that $\beta^{rp}(1 - f_1^{rp})$is identical for RLP and RCP of spheres, which may be coincidental, but the conjecture arises that $\beta^{rp}(1 - f_1^{rp})$ and C are constants (approximately 0.072 and -0.096, respectively) for random sphere packings, from loose to dense. For all crystalline packings it also turned out that C [and $\beta^{cp}(1 - f_1^{cp})$; see Eq. (9)] is identical, namely, $C = 1$ and $\beta^{cp}(1 - f_1^{cp}) = -0.75$ [1,2]. An identical C [or $\beta(1 - f_1)$] implies that the scaled bimodal packing fraction function, η/f_1, is the same.

For crystalline packings this value of C followed from the insight that the first derivative of the cell volume with respect to X_L at the large sphere side ($X_L = 1$) equals zero, so when a small sphere is inserted in any sphere in the packing, the sphere rattles [Eq. (8)]. This holds for all spheres in a crystalline lattice, which are all hyperstatic. In sc, bcc, and fcc structures the number of contacts (coordination number) z amounts to 6, 8, and 12, respectively. In random packings some spheres are in position where this principle also holds. It is, for instance, known that in random close packings locally crystalline arrangements can be found; near the RCP fraction limit of 0.64, the fraction of tetrahedra is for instance close to 1/3 [19,20]. Accordingly, to the isostatic ($z = 6$) and hyperstatic spheres ($z > 6$), Eq. (8) applies, the corresponding mean volume can be found in Fig. 2 ($C = 1$). But in random packings also hypostatic spheres ($z < 6$) contacts are found, for these spheres the *ansatz* is made:

$$\left.\frac{dV_{\mathrm{cell}}}{dX_L}\right|_{X_L=0} = 0. \tag{18}$$

Applying this boundary condition to Eq. (5) yields that $C = -1$ for these spheres; also this resulting volume can be found in Fig. 2, corresponding to an assembly of solely this type of spheres. Heuristically, the C pertaining to a random packing is thought of as the net effect of these two types of spheres present in a random arrangement. In other words, C (-0.096) of RCP is the statistical expectation of expansion (isostatic and hyperstatic) and contraction (hypostatic) generating spheres

$$\mathrm{C} = -\frac{4}{3}\beta^{rp}\left(1 - f_1^{rp}\right) = \frac{j - (n - j)}{n} = \frac{2j}{n} - 1, \tag{19}$$

where j is the number of spheres (in n) that behave as Eq. (8) and $n - j$ the number of spheres that obey Eq. (18), so j and n are both integers. In order to obtain Retger's equation ($C = 0$), Eq. (19) actually reveals that $j/n = 0.5$; i.e., the number of contraction and expansion generating spheres in a cluster are then equal. For RCP, on the other hand, substituting $C = -0.096$ (as $\beta^{\mathrm{rcp}} \approx 0.20$ and $f_1^{\mathrm{rcp}} \approx 0.64$) yields $j/n \approx 0.452$. It is noteworthy that this value of 0.452, based on β^{rcp} and f_1^{rcp}, is quite insensitive to the values that are taken for them. The value $f_1^{\mathrm{rcp}} \approx 0.64$ is generally accepted, but the value of β^{rcp} is less precisely known. Increasing and reducing its value with 10% and making use of Eq. (19) results in j/n values 0.447 and 0.457, respectively, so to a change of about 1% only. This implies that the assessment $j/n \approx 0.452$ is fairly robust.

Hence, from the current analysis it follows that the number of spheres that behave as Eq. (18) is slightly larger than the number of spheres that follow Eq. (8), i.e., $j < n/2$, which is needed to obtain a negative value of C, and hence the commonly observed volume contraction of bimodal random particle packings (yielding packing fraction increase). In computer-generated RCP of spheres, where the number of contacts is determined, it is also found that the total number of isostatic and hyperstatic spheres is approximately equal to the number of hypostatic spheres [10,11,14,16,17]. However, in these computer-generated packings mostly the number of hyperstatic spheres is slightly dominating, with which the present outcome seems not compatible, as here the hypostatic spheres seem to slightly dominate. It should also be mentioned that a majority of hypostatic spheres does not imply that the *mean* contact number ("coordination number") $\bar{z}$ is smaller than 6 as well, as part of the hyperstatic spheres may have 10 contacts or more [14,17], while by definition hypostatic spheres can at most have 5 contacts.

Furthermore, when $\beta^{rp}(1 - f_1^{rp})$ would be a constant for random packed spheres, as discussed above, it also follows that the percentage of hypostatic spheres in elementary clusters is the same as for RCP, namely, 55%, as j/n is then the same for all random packings [Eq. (19)]. In Ref. [49] it was derived that the mean geometrical coordination number $\bar{z}$, which includes the contacts with zero force, is approximately identical for all random packings. As these contacts are active when the monosized packing becomes bimodal, that is to say, when spheres start to differ in size, the present result indeed seems to be compatible with the aforesaid finding in Ref. [49].

In Ref. [46] a linear correlation has proposed between the mean contact number and packing fraction. In Ref. [49] the following linear relation between the mean number of mechanical contacts $\bar{Z}$, the number of contacts exerting force and contributing to the mechanical balance (hence $\bar{Z} \leqslant \bar{z}$), and random packing fraction was derived:

$$f_1^{rp} = \frac{\bar{Z}}{\bar{Z} + 2\sqrt{3}}, \tag{20}$$

with $\bar{Z}$ ranging from 4 (RLP) and 6 (RCP). Combining Eqs. (17) and (20) yields the following relation between β and $\bar{Z}$ for random sphere packings:

$$\beta^{rp} = \beta^{\mathrm{rcp}}(1 - f_1^{\mathrm{rcp}})\left(1 + \frac{\bar{Z}}{2\sqrt{3}}\right) = 0.072\left(1 + \frac{\bar{Z}}{2\sqrt{3}}\right). \tag{21}$$

From this equation it follows that there is linear relation between the mean number of mechanical contacts and the contraction coefficient β^{rp}.

For more than 60 years it has been conjectured that supercooled monatomic liquids, which resemble of random hard sphere packings, feature a universal structure [22–31]. Recent experimental observations of liquid lead [28] and of colloidal suspensions [30] confirm the presence of clusters, allowing a "structural" description of liquids'. Also molecular dynamics simulations reveal a nearly universal structure, comprising both icosahedral and polytetrahedral order in liquid copper [31]. The generated information about the magnitude of volume contraction and fraction of hypostatic spheres may serve in the search for the minimum number of spheres n that form a characteristic cluster of randomly packed spheres. For sc, bcc, and fcc structures n amounts to 8, 4, and 4, respectively [2]. The smallest integer combination that approximates the abovementioned j/n ratio (≈ 0.452) for random packings is 9/20. Accordingly, one could say that the current analysis reveals that 20 is a characteristic value for the *minimum* number of spheres n that would define a universal cluster of randomly packed monosized spheres. It is noteworthy that numerically generated RCP revealed typical complex polytetrahedral clusters, consisting of approximately 20 spheres as well [19–21], with which the present result is thus compatible. In Refs. [27,28] a typical *polytope* consisting of 120 atoms is mentioned.

IV. CONCLUDING REMARKS

The present paper reveals that the packing fraction of bimodal random arrangements of hard spheres with small diameter ratio (u) can be described with a similar model as for crystalline arrangements, presented in Refs. [1,2]. This packing fraction, Eq. (16), is characterized by a closed-form equation containing the concentration of the two components (actually by one of them, here the large one) and the sphere diameter ratio, and depends on two packing parameters, β and f_1. The new expression for the random packing of bimodal spheres, with small size ratio is compared extensively with RCP information from literature, empirically and computer generated, and good agreement is found. 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. For RCP both β and f_1 are all well-defined parameters with prescribed, so nonadjustable, values.

The concentration at which the packing fraction has an extremum is computed as a function of u. It appears that for the concerned number and volume concentrations, $X_L = k(u)$ and $c_L = h(u)$, respectively, hold that $k(u) + h(u) = 1$ and $k(u = 1) = 0.5$ (the content of large and small spheres being in parity). This expression is generic; i.e., it holds both for crystalline and random packings: In the former case the packing extremum constitutes a minimum, in the latter case it is a maximum packing fraction (for a given size ratio u).

The present approach also yields the characteristic volume of randomly packed bimodal spheres. This is governed by Eq. (5), applicable for n going to infinity, but also for a finite number of spheres n if random packings would have a repeatable structure (elementary cluster). The information on the RCP fraction increase by combining two sphere sizes, resulting in a mean volume change, provides information on the fraction of hypostatic spheres (and that of the other spheres: isostatic plus hyperstatic) in the random packing, which is about 55% (45%). This value is insensitive to the underlying values taken here for β^{rcp} and f_1^{rcp}, and also appears to be applicable to other random packing states such as RLP as it is conjectured that $\beta^{rp}(1 - f_1^{rp})$ is constant (≈ 0.072, and hence $C \approx -0.092$).

In the past it has been conjectured that glasses, supercooled monatomic liquids and colloidal suspensions, which resemble random hard sphere packings, are structurally organized. The current study yields insight into the minimum number of spheres involved in an elementary cluster, viz., 20 spheres, and it is tentatively concluded that this figure holds for all random packing states of identical spheres, which is compatible with the conclusion of Ref. [49] that all random sphere packing states possess approximately the same mean geometrical coordination number.

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APPENDIX

The first derivatives of Eq. (11) with respect to c_L and u read

$$\eta_{c_L} = \frac{d\eta}{dc_L} = \frac{C(u^3-1)\left[(c_L-1)^2u^3 - c_L^2\right]f_1}{[c_L(1-u^3)+u^3+C(1-c_L)c_L(u^3-1)]^2} \tag{A1}$$

and

$$\eta_u = \frac{d\eta}{du} = \frac{3Cu^2(1-c_L)c_Lf_1}{[c_L(1-u^3)+u^3+C(1-c_L)c_L(u^3-1)]^2}, \tag{A2}$$

respectively. The partial derivatives of Eq. (7) read

$$\eta_{X_L} = \frac{d\eta}{dX_L} = \frac{C(u^3-1)\left[X_L^2u^3-(1-X_L)^2\right]f_1}{[X_L(u^3-1)+1+CX_L(1-X_L)(u^3-1)]^2} \tag{A3}$$

and

$$\eta_u = \frac{d\eta}{du} = \frac{-3Cu^2X_L(1-X_L)f_1}{[X_L(u^3-1)+1)+CX_L(1-X_L)(u^3-1)]^2}. \tag{A4}$$

The number faction at which the bimodal packing has its extremum, $X_L = k(u)$, follows from

$$\frac{dk}{du} = \left.\frac{\eta_{X_L}}{\eta_u}\right|_{X_L=k} = \frac{(u^3-1)[(k^2u^3-(1-k)^2]}{-3u^2(1-k)k}. \tag{A5}$$

Equation (A5) transforms into Eq. (12) when k is replaced by $1-h$, implying that $h(u)+k(u)=1$. In Ref. [1], $k(u)$ was erroneously determined by solving $\eta_{X_L}=0$ [using Eq. (A3)], yielding

$$k(u) = \frac{1}{u^{\frac{3}{2}}+1}. \tag{A6}$$

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