Random packing fraction of binary similar particles:
Onsager’s model revisited

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Abstract

In this paper, the binary random packing fraction of similar particles with size ratios ranging from unity to well over 2 is studied. The classic excluded volume model for spherocylinders and cylinders proposed by Onsager [1] is revisited to derive an asymptotically correct expression for these binary packings. From a Taylor series expansion, it follows that the packing fraction increase by binary polydispersity equals 2f(1 - f)X1(1 – X1)(u – 1)^2 + O((u – 1)^3), where f is the monosized packing fraction, X1 is the number fraction of a component, and u is the size ratio of the two particles. This equation is in excellent agreement with the semi-empirical expression provided by Mangelsdorf and Washington [2] for random close packing (RCP) of spheres. Combining both approaches, a generic explicit equation for the bidisperse packing fraction is proposed, which is applicable to size ratios well above 2. This expression is extensively compared with computer simulations of the random close packing of binary spherocylinder packings, spheres included, and random loose sphere packings (1 ≤ u ≤ 2). The derived generic closed-form and parameter-free equation, which contains monosized void fraction, size ratio, and composition, appears to be in excellent agreement with the collection of computer-generated packing data using four different computer algorithms and RCP and random loose packing (RLP) compaction states. Furthermore, the present analysis yields a monodisperse packing fraction map of a wide collection of particle shapes at different compaction states. The explicit RCP-RLP boundaries of this map appear to be in good agreement with all reviewed data. The Appendix presents an review of published monodisperse packing fractions of (spher/o)cylinders for aspect ratios l/d from zero to infinity, and at RLP and RCP packing configurations, and they are related to Onsager’s model.
1. Introduction

The packing of granular matter is an old physical, biological and mathematical puzzle that has received much attention in the past millennia [3]. The packing fraction of particles, e.g. spheres, is the simplest example and is also one of the most basic feature of a granular matter system. Packing problems are ubiquitous and arise in transportation, agricultural, packaging and communication industries. Furthermore, attention has been paid to revealing the packing geometries and the route to understanding liquids, glasses, metals and metalloids, and granular materials. The packing of hard spheres is the simplest example of such systems, whether crystalline or amorphous. Besides being of scientific importance, the packing fraction of particles is also technically of relevance. Examples are concrete [4], ceramics [5], catalyst beds [6], coal-ore stackings [6, 7], composite materials [8, 9], fibrous filters [10], clothing materials, nonwovens and fibrous hygienic items [11], their technical properties depend to a considerable extent on the closeness of the packing of the particles.

The densest packing of equal particles is obtained for ordered (crystalline) arrangements or lattice packing, which can be computed. For example, for spheres, the dc (diamond cubic), sc (simple cubic), bcc, and fcc/hcp lattices have packing fractions of $3^{1/2}/\pi/16 \approx 0.34$, $\pi/6 \approx 0.52$, $3^{1/2}/\pi/8 \approx 0.68$, and $2^{1/2}/\pi/6 \approx 0.74$, respectively. For a disordered (random/amorphous) particle packing, the packing fraction depends on the densification state (e.g., loose and dense). Numerous numerical and experimental studies have confirmed a common upper limit for the random close packing (RCP) value of disordered frictionless sphere packings, $f_{\text{spe}}^{\text{rcp}}$, with a consistent value of approximately 0.64 [2, 5-7, 12-22]. Mathematically, the RCP state is difficult to define because by introducing order, higher packing factions can be obtained. In [3, 23] the “maximum random jammed” (MRJ) state was introduced as a concept, defined by configurations with minimal values of typical order parameters. For the strictly jammed packing, the lowest ordering yielded a packing fraction of 0.64. For random loose packing (RLP) of monodisperse particles, a reproducible packing fraction is also found [6, 13, 20, 24-29], for spheres $f_{\text{spe}}^{\text{rlp}} \approx 0.54$, which is a generally accepted value for this lower packing limit. In [3, 23], it was shown that strictly jammed sphere packings may reach a packing fraction as low as 0.49, but also that this comes with higher ordering. These sphere packings are members of a whole family of particle shapes, each having their characteristic loosest and densest packing configuration. Members of this family include spherocylinders, cylinders (with planar ends), cubes (and the four other platonic solids), etc.
When uniformly shaped particles of different sizes are randomly packed, *i.e.* generating a polydisperse packing, the packing fraction increases compared with the monosized packing, that is, the packing of congruent (or identical) particles, and the associated volume contraction depends on the particle size distribution. By combining two equally shaped (similar) particles of different sizes, such a polydisperse packing can be readily assembled. In this study, this specific polydisperse particle packing is analyzed, *viz.* the packing of two discretely sized and equally shaped particles, referred to as binary mixtures. Binary packing of similar particles was studied in [2, 5, 14, 16, 18, 30-33]. For binary mixes with a large size ratio \( u \) \( (u \to \infty) \), *i.e.* two noninteracting fractions, an analytical expression for the binary void fraction is available [18, 35, 36]. In [31, 32], analytical equations were derived for the packing fraction of crystalline structures consisting of randomly placed bidisperse hard spheres for the other limit, *viz.* a size ratio \( u \) close to unity \( (u \to 1) \). It was shown that the underlying approach for studying volume distortion introduced by unequal sphere pairs is also applicable to randomly packed spheres [33], yielding an analytical expression for the binary packing fraction for this limit. Furthermore, though the binary packing of similar particles with small size difference is relatively simple polydisperse system, it forms the basis of the packing description of polydisperse arrangements, for instance with geometric and binomial size distributions [34]. They can be statistically described by considering all binary combinations of the particle size classes present [34], so an accurate packing fraction description of each binary combination is crucial.

Here, the packing fraction of random binary similar particles with small size differences is revisited using Onsager’s model of excluded volume. Onsager developed this original model, for the isotropic liquid-to-nematic (I-N) phase transition of hard rod-like (spherocylinders and cylinders) particles, which was published in his seminal paper in 1949 [1]. This excluded volume concept was introduced by Kuhn in 1934 to study polymeric chains [37]. Onsager demonstrated that a phase transition can be predicted based on two-particle (spherocylinders or cylinders) interactions, represented by the second virial term in an expansion of the free energy of the system. The Onsager expressions for the excluded volume have mostly been used to study the packing of monosized particles, although his model allows for two (sphero)cylinders with different diameters and lengths. The polydisperse model has been used to study the phase transitions of particles of different lengths [38-40], diameters [41], or constant volumes [42]. To the best of the author’s knowledge, Onsager’s model has not yet been used to study the packing of binary particles. Specifically, the packing of binary similar particles, *i.e.* particles
with the same aspect ratio (length-diameter), is the topic of this study. The present paper focuses on packing fraction only, that is the ratio of the volume of the particles to the total volume they occupy, which is the primary feature of a particle assembly.

The remainder of this paper is organized as follows. In Section 2, Onsager’s excluded volume of monosized and binary pairs of (sphero)cylinders is revisited. Using a statistical approach, these expressions are used to derive a closed-form expression for the binary packing fraction of the aforementioned particles. It appears that the expressions for spherocylinders and cylinders are identical irrespective of their aspect ratio. The variation in the monosized packing fraction by binary polydispersity is a function of the concentration product $X_1(1 - X_1)$ and is proportional to the square of the relative size difference $u - 1$. In Section 3, a semi-empirical expression concerning the RCP fraction of binary spheres, based on the contraction function presented by Mangelsdorf and Washington [2], is introduced. It is shown that for $u \rightarrow 1$, this semi-empirical expression transforms into the expression obtained in Section 2, based on Onsager’s model. As Onsager’s model also allows for binary packings other than spheres, this semi-empirical expression for the RCP of spheres is generalized by introducing the factor $(1 - f)$ that follows from the Onsager-based model (Section 2). The quadratic expressions obtained in $(u - 1)$ are also compared with the first-order expressions originally proposed in [33]. In Section 4, this new expression is compared with the computationally generated RCP of spherocylinders including spheres. A comparison with the RLP of spheres, the latter having $(1 - f)$ which is approximately 25% larger than that of the RCP of spheres, is also presented. These comparisons yield excellent agreement over the entire compositional range and size ratios $u$ well beyond 2.

In Section 5 the simulations, both RLP and RCP, are further analyzed by scaling the results, and comparing them with the present model, and illustrating the effect of the contraction functions from [1], [2] and [33]. The packing fraction increase by binary polydispersity is governed by the factor $f(1 - f)$. Based on a literature review, the magnitude of this factor for a number of particle shapes and packing configurations (from loose to dense) is analysed in Section 6. The conclusions are collected in Section 7. While this paper focuses on bidisperse packings, the Appendix presents a review of monodisperse (sphero)cylinders packings. The Appendix reveals that for monodisperse packings, Onsager model is qualitatively correct. This is no surprise, as the model applies to colloids in thermal equilibrium. Despite this observation, this paper yields the important conclusion that applying the model yields a parameter-free closed-form expression that predicts the effect of bidispersity on packing fraction correctly.
To summarize, by revisiting and extending Onsager’s model to binary particle packings, a generic and accurate packing expression is obtained that is applicable to size ratios of at least 2, RLP and RCP, and a large collection of different spherocylinders. Hence, Onsager’s classical work contains much more information and has a wider application than what is generally appreciated.
2. Binary random packings of (sphero)cylinders

In this section, the binary packing of similar cylinders and spherocylinders is analyzed, viz. the packing of two discretely sized particles of equal shape, termed binary mixtures, using the theory of excluded volume by Onsager [1] developed for randomly oriented (sphero)cylinders. Zocher [43] discovered that colloidal solutions of rod-like particles undergo phase transition when they exceed a critical concentration. They provide a good model for liquid crystals, and Onsager realized that a system of hard rods can transition from the isotropic phase to the nematic phase when the density is sufficiently increased. Furthermore, based on the insight that only two-body interactions were necessary to explain this isotropic-nematic (I-N) transition, he developed a physically and mathematically lucid model based on the volume of the two particles and their excluded volume. The results of Onsager’s model are of great fundamental interest, and they have also proven to be useful for studying percolation [44, 45] and monodisperse particle packing [46]. First, the packing fraction of both monodisperse spherocylinders and cylinders is recapitulated, and subsequently, for the first time, Onsager’s model is applied to the binary packing case.

2.1 Monodisperse packings

Here, the case of monosized (congruent) cylinders and spherocylinders is considered. Both are centrally symmetric particles with diameter d, length l, and aspect ratio l/d, and the spherocylinders are capped at both ends by hemispheres with diameter so that their total length is l + d. The volumes of two of these particles are given by:

\[ 2V_{spc} = \frac{\pi d^3}{3} + \frac{\pi d^2 l}{2}, \]

(1)

and

\[ 2V_{cyl} = \frac{\pi d^2 l}{2}, \]

(2)

for spherocylinders and cylinders, respectively.

To assess the volume occupied by the two particles, Onsager computed the orientationally averaged excluded volume, \( V_e \). This is the volume that is inaccessible to one particle because
of the presence of the other, which depends on the particle size and shape. This excluded volume of the particle pair, see Figure 1, is given by [1]

\[ V_{e,spc} = \frac{4\pi d^2}{3} + 2\pi d^2 l + \frac{\pi d^2 l}{2}, \tag{3} \]

and

\[ V_{e,cyl} = \frac{\pi^2 d^3}{8} + \frac{\pi(\pi+3) d^2 l}{4} + \frac{\pi d l^2}{2}, \tag{4} \]

for spherocylinders and cylinders, respectively. The latter term in Eqs. (3) and (4) lead when l/d is large and is identical for spherocylinders and cylinders. As said, both equations follow from averaging the relative orientations [1]. In Figure 1 the concept particle packing and excluded volume is graphically explained, taking monosized spheres as example. The packing fraction is the ratio of the volume of the particles to the total volume they occupy.

Onsager derived the excluded volume to assess the phase transitions, which are concentration-related in liquid crystals. Therefore, following the approach of Onsager [1], the packing fraction of the (sphero)cylinders is defined by the particle volume and excluded volume:

\[ f_{spc} = \frac{2V_{spc}}{V_{e,spc}}, \quad f_{cyl} = \frac{2V_{cyl}}{V_{e,cyl}}. \tag{5} \]

The excluded volume holds for a pair of particles, so in Eq. (5), two particle volumes need to be taken to assess the packing fraction. Eqs. (1) and (3) into Eq. (5), yields

\[ f_{spc} = \alpha \left( \frac{1 + \frac{2\alpha}{3}}{1 + 4\alpha + \frac{8\alpha^2}{3}} \right) = \left( \frac{\alpha^{-1} + \frac{2}{3}}{\alpha^{-2} + 4\alpha^{-1} + \frac{\pi}{3}} \right), \tag{6} \]

for spherocylinders, substituting. Substituting Eqs. (2) and (4) into Eq. (5) yields

\[ f_{cyl} = \alpha \left( 1 + \frac{(\pi+3)\alpha}{2} + \frac{\pi\alpha^2}{4} \right)^{-1} = \alpha^{-1} \left( \alpha^{-2} + \frac{(\pi+3)\alpha}{2\alpha} + \frac{\pi}{4} \right)^{-1}, \tag{7} \]

for cylinders, in which the following aspect ratio has been introduced
\[ \alpha = \frac{d_1}{d} . \] (8)

In the Appendix the (sphero)cylinder packing expressions, Eqs. (6) and (7), provided by using the excluded volume expressions of Onsager, are compared with experimental and computational data for a wide range of \( \alpha \), both for RCP and RLP configurations.

The packing of monosized spheres, the volume fraction occupied by the spheres is the packing fraction (the space in between is the void fraction), and the excluded volume of the pair of filled spheres is encircled by a dashed line.

It is seen that both expressions characterize the observed trends with respect to \( \alpha \) quite well, and both equations appear to be in qualitative agreement with published data on monodisperse particles. With a slight modification, they are in good agreement in the entire aspect ratio range \( (0 \leq \alpha \leq \infty) \). In what follows, the effect of bidispersity on packing fraction is quantified, again using the excluded volume theory of Onsager.

### 2.2 Particle volume of binary assemblies

Here, the case of binary packing of (discretely sized) similar cylinders and spherocylinders is considered, with a normalized number distribution

\[ P(d) = X_1 \delta(d - d_1) + X_2 \delta(d - d_2) . \] (9)
where \( \delta \) indicates the Dirac delta function, and \( X_1 \) and \( X_2 \) are the number fractions of the two components, for which holds

\[
X_1 + X_2 = 1; X_1^2 = X_1 - X_1X_2; \quad X_2^2 = X_2 - X_1X_2 ,
\]

(10)

where \( d \) denotes the particle diameter. As we study an assembly of two particle sizes with the same shape (but different size), all dimensions have an identical size ratio \( u \), so:

\[
d_1 \quad \frac{l_1}{l_2} = u; \quad \frac{V_{1,\text{spc}}}{V_{2,\text{spc}}} = \frac{V_{1,\text{cyl}}}{V_{2,\text{cyl}}} = u^3 .
\]

(11)

It also implies that small and large particles also possess identical aspect ratios. The mean volume sizes of the two spherocylinders (see Eq. (1)), is

\[
2V_{\text{spc}} = \left(\frac{\pi d_1^3}{3} + \frac{\pi d_1^2 l_1}{2}\right)X_1 + \left(\frac{\pi d_2^3}{3} + \frac{\pi d_2^2 l_2}{2}\right)X_2 = 2V_{2,\text{spc}}(u^3 X_1 + X_2) = 2V_{2,\text{spc}}(1 + (u^3 - 1)X_1) \quad ,
\]

(12)

and the mean particle volumes of the two cylinders, as shown in Eq. (2), reads

\[
2V_{\text{cyl}} = \frac{\pi d_1^3}{2}X_1 + \frac{\pi d_2^3}{2}X_2 = 2V_{2,\text{cyl}}(u^3 X_1 + X_2) = 2V_{2,\text{cyl}}(1 + (u^3 - 1)X_1) \quad ,
\]

(13)

where Eqs. (10) and (11) have been applied.

### 2.3 Excluded volume of binary (sphero)cylinders

In addition to the well-known expression for the excluded volume of monosized (sphero)cylinders, Onsager also provided expressions for the orientally averaged excluded volume of two (sphero)cylinders with unequal lengths and diameters.

For spherocylinders this equation ("Eqs. (A15)-(A16)" [1]) reads:

\[
V_{e,\text{spc}}^{1,2} = \frac{\pi(d_1+d_2)^3}{6} + \frac{\pi(d_1+d_2)^2(l_1+l_2)}{4} + \frac{\pi(d_1+d_2)l_1l_2}{4} = (u + 1)^3 \frac{\pi d_2^3}{6} + (u + 1)^3 \frac{\pi d_2^3 l_2}{4} + u(u + 1) \frac{\pi d_2^2 l_2}{2} \quad ,
\]

(14)
see Eq. (11). For \( d_1 = d_2 \) and \( l_1 = l_2 \), and hence \( u = 1 \) and \( V_{e,\text{spc}}^{1,1} = V_{e,\text{spc}}^{2,2} \), and Eq. (14) can be reduced to Eq. (3) for the two mono-sized spherocylinders. The mean excluded volume of the assembly by randomly mixing the two particle sizes follows from the statistically probable combinations of small and large (sphero)cyinders as follows:

\[
V_e = \sum_{i=1}^{2} \sum_{j=1}^{2} X_i X_j V_e^{i,j} = X_1 V_e^{1,1} + X_2 V_e^{2,2} - X_1 X_2 (V_e^{1,1} + V_e^{2,2} - V_e^{1,2} - V_e^{2,1}) \, ,
\]

(15)

whereby Eq. (10) was used. In view of Eqs. (10) and (11), and because

\[
V_e^{1,1} = u^3 V_e^{2,2} ; \quad V_e^{2,1} = V_e^{1,2} \quad ,
\]

(16)

Eq. (15) becomes

\[
V_e = (1 + (u^3 - 1)X_1)V_e^{2,2} - X_1 (1 - X_1)((u^3 + 1)V_e^{2,2} - 2V_e^{1,2}) \, .
\]

(17)

Furthermore, for spherocylinders holds

\[
((u^3 + 1)V_{e,\text{spc}}^{2,2} - 2V_{e,\text{spc}}^{1,2}) = \left( \pi d_2^3 + \frac{3\pi d_2 l_2}{2} + \frac{\pi d_2 l_2^2}{2} \right) (u + 1)(u - 1)^2 =
\]

\[
(V_{e,\text{spc}}^{2,2} - 2V_{e,\text{spc}}^{1,2})(u + 1)(u - 1)^2 \, ,
\]

(18)

see Eqs. (12) and (14).

For the excluded volume of two cylinders with different \( d \) and \( l \) values, the following expression (“Eq. (A14)” [1]) was provided:

\[
V_{e,\text{cyl}}^{1,2} = \frac{\pi^2 d_1 d_2 (d_1 + d_2)}{16} + \frac{\pi (d_1^2 d_2 + d_2^2 d_1)}{8} + \frac{\pi d_1^2 d_2 (l_1 + l_2)}{8} + \frac{\pi d_1 d_2 (l_1 + l_2)^2}{4} =
\]

\[
u(u + 1) \frac{\pi^2 d_2^3}{16} + \left[ 2(u^3 + 1) + u(u + 1)(\pi + 1) \right] \frac{\pi d_2 l_2}{8} + u(u + 1) \frac{\pi d_2 l_2^2}{4} \, ,
\]

(19)

see Eq. (11). It can be readily observed that Eq. (19) can be transformed into Eq. (4) for \( u = 1 \), that is, when \( d_1 = d_2 \) and \( l_1 = l_2 \). Combining Eqs. (13) and (19) yields

\[
((u^3 + 1)V_{e,\text{cyl}}^{2,2} - 2V_{e,\text{cyl}}^{1,2}) = \left( \frac{\pi^2 d_2^3}{8} + \frac{\pi (u+1) d_2 l_2}{4} + \frac{\pi d_2 l_2^2}{2} \right) (u + 1)(u - 1)^2 =
\]

(20)
Note that the analysis of bidisperse spherocylinders and cylinders yields Eqs. (18) and (20), respectively, which are very similar.

2.4 Packing fraction of binary (sphero)cylinders

For convenience, by definition, \( X_1 \) is henceforth assigned to the number fraction of the large component \( X_L \), and hence \( u \geq 1 \) (Eq. (11)). The binary packing fraction \( \eta \) follows from Eqs. (5), (12), (17), and (18) for spherocylinders, and Eqs. (5), (13), (17), and (20) for cylinders, where the nominator and denominator are divided by \( V_{e,cyl}^{2,2} \), yielding the following binary packing fraction that is a function of composition, size ratio and monodisperse packing fraction:

\[
\eta(u, X_L) = \frac{f[1 + X_L(u^3 - 1)]}{1 + X_L(u^3 - 1) \cdot (1 - f)X_L(1 - X_L)v(u)}, \tag{21}
\]

with as contraction function:

\[
v(u) = (u + 1)(u - 1)^2. \tag{22}
\]

The function \( v(u) > 0 \) governs the decrease in the denominator, which reflects the contraction of the packing volume. For \( v(u) = 0 \), the binary packing fraction would take the monosized value \( f \), see Eq. (21), and for \( v(u) > 0 \), the bidisperse packing fraction \( \eta(u, X_L) \) exceeds this monodisperse value (i.e., bidisperse implies that \( u > 1, X_L \neq 0, \) and \( X_L \neq 1 \)).

Expressed in large particle volume fraction \( c_L \), that is volume of large particles divided by volume of large and small particles (such that \( c_L + c_S = 1 \)), Eq. (21) reads

\[
\eta(u, c_L) = \frac{f[c_L(1 - u^3) + u^3]}{c_L(1 - u^3) + u^3 \cdot (1 - f)c_L(1 - c_L)v(u)}, \tag{23}
\]

as the number fraction \( X_L \) is related to this volume fraction \( c_L \) by:

\[
X_L = \frac{c_L}{(1 - c_L)u^3 + c_L}. \tag{24}
\]
Based on the equations of excluded volume by Onsager for pairs of spherocylinders and cylinders and their statistical occurrence in a two-component mix, one analytical expression for their binary packing fractions is derived for both particle shapes. It follows that for spherocylinders and cylinders, irrespective of their aspect ratio $\alpha (d/l)$, an identical expression follows for the bidisperse packing fraction, viz. Eqs. (21)-(23), which is the reason why in this general expression $\eta$ is not bearing the subscript “spc” or “cyl”. This equation furthermore shows that the deviation of the monosized packing fraction is of the order of $(u - 1)^2$. In studying the (I-N) phase transitions of polydisperse solutions of rods with slightly different lengths, Chen [40] also found a second-order dependency on the scaled distribution width.

Furthermore, although the aspect ratio and particle shape (cylinder or spherocylinder) indirectly affect the monosized packing fraction $f$, they are not independent factors in the binary packing expression (Eq. (21)). Eqs. (21) and (23) also reveal that the volume contraction depends on the product of large and small fractions ($c_L(1 - c_L)$ or $X_L(1 - X_L)$). In [33] it was shown that the packing fraction of bidisperse packings with small size difference can be described with a similar model as for crystalline arrangements [31, 32], yielding Eqs. (21) and (23) as well. The derivation was based on counting the number of unequal (that is large-small particle) contacts in these packings, which resulted in the same product of large and small fractions. It is remarkable that, the combination of Onsager’s expressions for the excluded volume of two particles, in combination with the statistical occurrence of equal and unequal particle pairs (Eq. (15)), result in the same bidisperse packing expressions that only differ in $v(u)$. 
3. Comparison with semi-empirical model of RCP of spheres

In the previous section, a closed-form expression was derived for the binary packing fraction section when the size difference was small (the size ratio was close to unity). To this end, the excluded volume theory of Onsager was employed, and identical expressions were obtained for the binary cylinder and spherocylinder assemblies.

In this section, this generic equation is compared with a bidisperse packing expression, which follows from revisiting a paper in which a semi-empirical expression is proposed based on random close ball packings [2]. Balls (or spheres) are spherocylinders for which \( l/d = 0 \) (or \( \alpha^{-1} = 0 \)), see Eq. (8).

3.1 Semi-empirical model of RCP of spheres

Binary packing experiments combined a large ball \( (V_{1,spe} = 0.408 \text{ cc}) \) with three smaller balls \( (V_{2,spe} = 0.260 \text{ cc}, 0.1705 \text{ cc}, \text{ or } 0.1032 \text{ cc}) \), as reported in [2]. The corresponding volume ratios \( u_3 \) were 1.57, 2.39, and 3.95, yielding size ratios of \( u = 1.16, 1.34, \text{ and } 1.58 \), respectively. The volume occupied by the balls was divided by the total number of balls, and this compared with the volume occupied by a ball in the monosized case. In these monodisperse packings of balls with volumes 0.408 cc, 0.260 cc, 0.1705 cc, and 0.1032 cc, the volume occupied per ball was 0.642 cc (“\( V_1 \)”), 0.406 cc, 0.266 cc, and 0.160 cc (“\( V_2 \)”), respectively. Because \( f \) corresponds to the ratio of \( V_{1,spe} \) and “\( V_1 \)” and of \( V_{2,spe} \) and “\( V_2 \)”, their monosized packing fraction follows \( f \approx 0.64 \), implying that the RCP conditions were met. Remarkably, they published this value in September 1960 [2], later than [7] dated May 1960, but earlier than [13] dated December 1960. Also for the composed binary mixes, the total packing volume was measured, and compared to the volume which would be expected based on the monosized packing values. The average volume reduction per ball was computed and denoted by \( V_{xs} \), for which the following semi-empirical expression was proposed:

\[
V_{xs} = 4C \frac{(V_{1,spe} - V_{2,spe})^2}{f_{spe}^{rcp}(V_{1,spe} + V_{2,spe})} X_1 X_2 , \tag{25}
\]

with \( C = 0.0195 \) as the fitting parameter. The factor \( f_{spe}^{rcp} \) is introduced here, which is the ratio of \( V_{1,spe} \) and “\( V_1 \)” and of \( V_{2,spe} \) and “\( V_2 \)”, as “\( V_1 \)” and “\( V_2 \)” where used in [2]. Contraction function (25) illustrates that for random binary mixtures, the volume of the packing contracts; hence, the packing fraction is higher than the monosized value. Following the experimental
interpretation described in [2], the binary packing fraction can be mathematically formulated as:

\[ \eta_{\text{spe}}^{\text{rcp}} = \frac{(N_1 V_{1,\text{spe}} + N_2 V_{2,\text{spe}})}{(N_1 V_{1,\text{spe}} + N_2 V_{2,\text{spe}})/\eta_{\text{spe}}^{\text{rcp}} - (N_1 + N_2)V^{\text{xs}}}, \]  

(26)

where \( N_1 \) and \( N_2 \) are the numbers of large and small balls in the packing, respectively, \( V^{\text{xs}} \) is the volume reduction per ball, and the last term of the dominator is the volume contraction. The number fraction follows from:

\[ X_1 = \frac{N_1}{N_1 + N_2}, \]  

(27)

when \( N_1 + N_2 \to \infty \) (the infinite volume limit). The volume ratio is

\[ \frac{V_{1,\text{spe}}}{V_{2,\text{spe}}} = u^3. \]  

(28)

With Eqs. (27) and (28), Eq. (26) can be rewritten as

\[ \eta_{\text{spe}}^{\text{rcp}}(u, X_L) = \frac{\eta_{\text{spe}}^{\text{rcp}}[1 + X_L(u^3 - 1)]}{1 + X_L(u^3 - 1) - 4CX_L(1 - X_L)} \left( \frac{u^3 - 1}{u^3 + 1} \right). \]  

(29)

Therefore, it appears that the empirical approach of [2] results in the same type of equation as that theoretically derived here (Eqs. (21)), and previously in [33]. Note however that Eq. (29) is applicable to larger size ratios, \( i.e. \ u = 1.6 \), and not only for \( u - 1 \approx 0 \).

The one-page paper by Mangelsdorf and Washington [2] is quite brief and does not specify the experimental conditions that underlie Eq. (25), and the equation that relates it to the binary packing fraction (Eq. (26)) is not provided. This brevity may be the reason why this original paper seems to have fallen somewhat into oblivion [47].

3.2 Model comparison

Eqs. (21) and (22), based on the application of Onsager’s model to similar (sphero)cylinders, and Eq. (29) for RCP of spheres, derived from [2] are very similar; they differ only in the volume contraction term, which is the last term of the denominator, in particular the contraction...
function $v(u)$. It is also noteworthy that in [33], the same type of function was derived, with a contraction function that was linear in $(u^3 - 1)$. To compare Eqs. (21), (22), and (29) in the vicinity of $u = 1$, they are asymptotically approximated using the 3rd polynomial of the Taylor series in variable $u$:

$$\eta(u, X_L) = \eta(1, X_L) + \eta_u(u, X_L) (u - 1) + \frac{1}{2} \eta_{uu}(u, X_L) (u - 1)^2 + O((u - 1)^3),$$  \hspace{1cm} (30)

yielding

$$\eta(u, X_L) = f + 2f(1 - f)X_L(1 - X_L)(u - 1)^2 + O((u - 1)^3),$$  \hspace{1cm} (31)

and

$$\eta_{\text{spe}}^{\text{rcp}}(u, X_L) = f_{\text{spe}}^{\text{rcp}} + 36C f_{\text{spe}}^{\text{rcp}}X_L(1 - X_L)(u - 1)^2 + O((u - 1)^3),$$  \hspace{1cm} (32)

respectively. It follows that both equations are very similar and give a quadratic deviation in $(u - 1)$ of the monosized packing fraction. Both equations are in quantitative agreement if

$$18C = 1 - f_{\text{spe}}^{\text{rcp}}.$$  \hspace{1cm} (33)

This equality can be verified by computing $18C \approx 0.35$ and $1 - f_{\text{spe}}^{\text{rcp}} \approx 0.36$, which are very close and within the experimental accuracy. Accordingly, it follows that for bidisperse mixes with small size differences, the semi-empirical fit based on bidisperse random close-packed spheres tends to the same theoretically derived equation based on Onsager’s model for bidisperse (spherocylinders). Eq. (33) also implies that the fitting parameter $C$ in [2] is mathematically related to $(1 - f_{\text{spe}}^{\text{rcp}})$. Furthermore, it also follows that Eqs. (29), which was originally derived for the RCP of spheres only, can therefore be generalized to Eq. (21) but with the contraction function

$$v(u) = \frac{4(u^3 - 1)^2}{9(u^3 + 1)}.$$  \hspace{1cm} (34)

This means that in Eq. (29), $C$ is replaced by $(1 - f_{\text{spe}}^{\text{rcp}})/18$, as shown in Eq. (33). In view of Eq. (33), Eqs. (21) and (34) are transformed into Eq. (29) when $f = f_{\text{spe}}^{\text{rcp}} \approx 0.64$, i.e. the original
equation proposed in [2], derived for the RCP of spheres. However, the combination of Eqs. (21) and (34) may also allow for the application of Eq. (29) to packings other than the RCP of spheres, such as (sphero)cylinders and looser packings, which are verified in detail in the following subsections.

In [33], as contraction function $v(u)$ was put forward

$$v(u) = 4\beta (u^3 - 1)/3 = 4\beta (u^2 + u + 1)(u - 1)/3 \quad ,$$

(35)

with $\beta \approx 0.20$ for the RCP of spheres [33]. At the limit of $u \to 1$, Eqs. (21), (30), and (35) yield

$$\eta(u, X_L) = f + 4\beta f(1 - f)X_L(1 - X_L)(u - 1) + O((u - 1)^2) \quad .$$

(36)

The models derived from the Onsager and Mangelsdorf and Washington models yield second-order terms in $(u - 1)$ (Eqs. (31) and (32)), the equation proposed in [33] yields an approximation of the packing fraction increase that is linear in $u - 1$ for $u \downarrow 1$.

![Figure 2](https://example.com/figure2.png)

**Figure 2** Contraction functions $v(u)$ as a function of the size ratio $u$, $u$ ranging from unity to two, computed using Eqs. (22), (34) and (35), in the latter $\beta = 0.20$ is employed [33].

This linear relation was already proposed in [48], in which $(u^2 + u + 1)/3$ was replaced by unity as $u \downarrow 1$. In [48], product $c_L(1 - c_L)$ was used in Eq. (36) instead of $X_L(1 - X_L)$; however, for $u \downarrow 1$, $X_L \to c_L$, see Eq. (24).
To illustrate the difference between using $v(u)$ given by Eqs. (22), (34), and (35), $v(u)$ is shown in Figure 2. The difference in $v(u)$ predicted by the Onsager and Mangelsdorf and Washington models for a given $u$ is very minor for a small $u - 1$, which is not surprising, as both Eqs. (22) and (34) tend to $2(u - 1)^2$ for $u \to 1$. However, for a larger $u$, the difference becomes more pronounced, and at $u = 2$, it is approximately 25%.

Figure 2 also shows that the contraction function linear in $(u^3 - 1)$, in Eq. (35), is close to the second-order models based on the Onsager model and Mangelsdorf and Washington experiments but is less accurate in the entire range of $1 \leq u \leq 2$. For a small $u - 1$, owing to its linear dependence on $u - 1$, it overestimates the contraction (and packing fraction), whereas for $u \to 2$ and larger, it underestimates the volume contraction.

From the foregoing, it follows that the derivation of the Onsager theory-based model and the derivation of the Mangelsdorf and Washington data-based model yield similar equations. The former yields the introduction, in view of Eq. (33), of the term $(1 - f)$ in Eq. (29).

To assess both models, each of which has a different contraction function $v(u)$, viz. Eq. (22) and (34), in the next section, they are compared with a broad set of modern numerical packing simulations of the RCP, spherocylinders, and RLP of spheres.
4. Simulated random packing fraction of bidisperse spherocylinders

In this section, Onsager- and Mangelsdorf and Washington-based models are compared to computer-generated packing of bidisperse random packings: close-packed spheres (RCP), $f_{\text{spe}}^{\text{RCP}} \approx 0.64$, close-packed spherocylinders ($l/d > 0$) with different aspect ratios, and random loose packed spheres (RLP), $f_{\text{spe}}^{\text{RLP}} \approx 0.54$. Note that the sphere packings are spherocylinder packings in the special case where $l/d = 0$. The simulation results of four different computational protocols are used.

4.1 Computer generated RCP of spheres

In [33] the derived expression for the binary packing fraction, linear in $u^3 - 1$ (Eq. (35)), was extensively compared with a broad collection of computational and experimental packing data, which were available for $u = 2$ only. These packing fraction values were in line with each other, but for a solid verification also accurate packing fractions for $u < 2$ are required. To this end, in Table 1, computer-generated data [49-51] concerning the bidisperse RCP of spheres are included for $u = 1.3, 1.5, 1.7$, and $2$ versus the volume fraction $c_L$ of large spheres. Note that for these larger $u$ values, $O(u - 1) \approx 1$; therefore, it is no longer close to zero. The data from [49] are generated with the same model as referred to in [17], [50] with the model of [19, 21], and [51] with the model described in [20]. The three referenced sources report slightly different monosized RCP fraction values ($f_{\text{spe}}^{\text{RCP}}$), viz. 0.644 [49], 0.643 [50], and 0.634 [51], which follow from $\eta_{\text{spe}}^{\text{RCP}}(u, c_L = 0)$ or $\eta_{\text{spe}}^{\text{RCP}}(u, c_L = 1)$ (Table 1). Therefore, their binary packing fraction values, $\eta_{\text{spe}}^{\text{RCP}}$, are all divided (scaled) by their monosized packing value, $f_{\text{spe}}^{\text{RCP}}$, which are included in Figure 3. First, all simulation models yield scaled binary packing fraction values that are very close to each other.

In Figure 3, Eq. (23) is set out versus $c_L$ for $u = 1.3, 1.5, 1.7$ and $2$, using both Eqs. (22) and (34), that is, the contractions following the analyses of Onsager’s model and Mangelsdorf and Washington’s empirical fit. For the smallest $u, u = 1.3$, both models are very close, as expected, in view of their identical asymptotic behavior for $u \downarrow 1$. For larger $u$, it can be seen that the Onsager contraction function results in a much larger binary packing fraction than experimentally expected and simulated.

The figure also confirms that Eqs. (23) and (34) can adequately predict the scaled binary RCP fraction over the entire compositional range of $0 \leq c_L \leq 1$ and for the size ratio range of $1 \leq u \leq 2$. This expression, a combination of the Onsager- and Mangelsdorf and Washington-based
expressions, is highly accurate and useful in predicting the binary packing fraction, even up to a size ratio $u$ of (at least) 2. This figure confirms that the use of Eq. (34) in Eq. (23) provides a better agreement than Eq. (22), and this performance becomes more evident for a larger $u$.

| $c_l$ | $u = 1.3$ | $u = 1.5$ | $u = 1.7$ | $u = 2$ |
|------|----------|----------|----------|--------|
| 0.0  | 0.6444   | 0.6444   | 0.6444   | 0.6444 |
| 0.1  | 0.6461   | 0.6478   | 0.6496   | 0.6519 |
| 0.2  | 0.6475   | 0.6510   | 0.6545   | 0.6593 |
| 0.3  | 0.6488   | 0.6538   | 0.6590   | 0.6662 |
| 0.4  | 0.6497   | 0.6561   | 0.6629   | 0.6726 |
| 0.5  | 0.6503   | 0.6578   | 0.6660   | 0.6782 |
| 0.6  | 0.6504   | 0.6586   | 0.6680   | 0.6823 |
| 0.7  | 0.6500   | 0.6582   | 0.6682   | 0.6841 |
| 0.8  | 0.6490   | 0.6563   | 0.6657   | 0.6819 |
| 0.9  | 0.6472   | 0.6520   | 0.6588   | 0.6718 |
| 1.0  | 0.6444   | 0.6444   | 0.6444   | 0.6444 |

| $c_l$ | $u = 1.3$ | $u = 1.5$ | $u = 1.7$ | $u = 2$ |
|------|----------|----------|----------|--------|
| 0.0  | 0.6434   | 0.6434   | 0.6434   | 0.6434 |
| 0.1  | 0.6476   | 0.6496   | 0.6475   | 0.6523 |
| 0.2  | 0.6479   | 0.6512   | 0.6510   | 0.6608 |
| 0.3  | 0.6492   | 0.6536   | 0.6546   | 0.6678 |
| 0.4  | 0.6500   | 0.6555   | 0.6588   | 0.6748 |
| 0.5  | 0.6507   | 0.6569   | 0.6634   | 0.6803 |
| 0.6  | 0.6505   | 0.6575   | 0.6656   | 0.6834 |
| 0.7  | 0.6502   | 0.6568   | 0.6671   | 0.6839 |
| 0.8  | 0.6491   | 0.6555   | 0.6652   | 0.6814 |
| 0.9  | 0.6474   | 0.6516   | 0.6556   | 0.6711 |
| 1.0  | 0.6437   | 0.6436   | 0.6443   | 0.6445 |

| $c_l$ | $u = 1.3$ | $u = 1.5$ | $u = 1.7$ | $u = 2$ |
|------|----------|----------|----------|--------|
| 0.0  | 0.6340   | 0.6340   | 0.6340   | 0.6340 |
| 0.1  | 0.6356   | 0.6372   | 0.6386   | 0.6404 |
| 0.2  | 0.6370   | 0.6401   | 0.6431   | 0.6469 |
| 0.3  | 0.6382   | 0.6423   | 0.6475   | 0.6534 |
| 0.4  | 0.6392   | 0.6453   | 0.6515   | 0.6597 |
| 0.5  | 0.6399   | 0.6472   | 0.6549   | 0.6657 |
| 0.6  | 0.6402   | 0.6484   | 0.6575   | 0.6708 |
| 0.7  | 0.6399   | 0.6484   | 0.6586   | 0.6743 |
| 0.8  | 0.6389   | 0.6468   | 0.6571   | 0.6743 |
| 0.9  | 0.6370   | 0.6426   | 0.6506   | 0.6661 |
| 1.0  | 0.6340   | 0.6340   | 0.6340   | 0.6340 |

**Table 1** Binary packing fraction $\eta_{\text{spe}}^{r_{\text{cp}}}(u, c_l)$ following from computer simulations of RCP of binary spheres with 4 different size ratios $u$; a) [49], b) [50], c) [51]. The table shows that these sources reported different monosized packing values ($f_{\text{spe}}^{r_{\text{cp}}}$), viz. 0.644 [49], 0.643 [50], and 0.634 [51]. The maximum packing values $\eta_{\text{spe, max}}^{r_{\text{cp}}}$ are indicated in bold.
Figure 3  Scaled packing fraction of randomly close packed binary spheres (size ratios $u = 1.3, 1.5, 1.7$ and $2$), $\eta_{\text{spe}}^{\text{rcp}}(u, c_L)/f_{\text{spe}}^{\text{rcp}}$, as a function of the large sphere volume fraction. The graph contains Eqs. (23), with either Eq. (22) or Eq. (34) substituted, and computer-generated data (listed in Tables 1 and 3 ($l/d = 0$)).

A comparison with the binary RCP of spheres for larger $u$ is offered by Desmond and Weeks [22]. They numerically generated polydisperse packings of spheres with different diameter-size distributions: binary, linear, Gaussian, and lognormal. The packing fractions of these different polydisperse packings were captured using a single equation containing the polydispersity (“δ”) and skewness (“S”). For the binary distribution, polydispersity and skewness are functions of the particle size ratio (“η”) and composition (“ρ”), see “Table I” [22]. In Table 2, the packing results of three of the generated binary packings are summarized [52].

| “δ” [22] | “S” [22] | $u$ [52] | $X_L$ [52] | $f_{\text{spe}}^{\text{rcp}}$ [52] | $f_{\text{spe}}^{\text{rcp}}$ (Eq. (34)) |
|----------|----------|----------|-----------|-----------------|-----------------|
| 0.4      | 1.5      | 2.27     | 0.20      | 0.683           | 0.685           |
| 0.4      | -0.5     | 2.70     | 0.62      | 0.653           | 0.668           |

Table 2  Computer simulation results of RCP fraction of binary spheres [22, 52], and the binary packing fraction using Eqs. (21) and (34), and $f_{\text{spe}}^{\text{rcp}} = 0.634$.

In this table, the binary packing fractions are included, according to Eqs. (21) and (34), which are based on the number fraction $X_L$, and using $f_{\text{spe}}^{\text{rcp}} = 0.634$ [22]. For $u = 2.27$, the agreement is still very good; however, for larger $u$ (2.63 and 2.70), the limitations of these equations become apparent.
4.2 Packings of spherocylinders

In this subsection, Eq. (23) is applied to the packing of binary spherocylinders with various aspect ratios, l/d. In the previous subsection, it was seen that Eq. (34) provides best agreement, and that Eq. (22) appears to overestimate the bidisperse packing fraction for u = 2. This is no surprise; in Figure 2, it can also be seen that both contraction functions v(u) also diverged towards u = 2. Accordingly, only Eq. (34) is used as the contraction function in Eq. (23).

In [53], dense binary packings of spherocylinders were numerically simulated for a size ratio u = 2 for aspect ratios (denoted as “w”) l/d = 0 (spheres), 0.1, 0.35, 1, 1.5, and 2. In Table 3, the packing fractions, read off from “Fig. 10a” [53], versus the large volume fraction c_L are summarized.

| c_L | d/l = 0 | d/l = 0.1 | d/l = 0.35 | d/l = 1 | d/l = 1.5 | d/l = 2 |
|-----|---------|-----------|------------|---------|-----------|---------|
| 0.0 | 0.645   | 0.672     | 0.686      | 0.659   | 0.643     | 0.629   |
| 0.1 | 0.653   | 0.678     | 0.691      | 0.667   | 0.651     | 0.638   |
| 0.2 | 0.660   | 0.683     | 0.696      | 0.673   | 0.658     | 0.644   |
| 0.3 | 0.664   | 0.686     | 0.700      | 0.680   | 0.664     | 0.652   |
| 0.4 | 0.669   | 0.690     | 0.702      | 0.684   | 0.668     | 0.656   |
| 0.5 | 0.672   | 0.693     | 0.705      | 0.687   | 0.671     | 0.659   |
| 0.55| 0.674   | 0.694     | 0.706      | 0.689   | 0.673     | 0.659   |
| 0.6 | 0.675   | 0.695     | 0.706      | 0.689   | 0.673     | 0.658   |
| 0.65| 0.676   | 0.693     | 0.704      | 0.688   | 0.673     | 0.658   |
| 0.7 | 0.675   | 0.692     | 0.704      | 0.687   | 0.672     | 0.657   |
| 0.8 | 0.671   | 0.687     | 0.700      | 0.681   | 0.665     | 0.649   |
| 0.9 | 0.664   | 0.680     | 0.694      | 0.672   | 0.657     | 0.635   |
| 1.0 | 0.645   | 0.672     | 0.686      | 0.659   | 0.643     | 0.629   |

Table 3 Binary packing fraction η_{sph}^{rcp}(u, c_L) following from computer simulation of RCP of spherocylinders with six different aspect ratios l/d and size ratio u = 2, derived from “Fig. 10a” of [53].

Their obtained f_{sph}^{rcp} of the RCP of monodisperse spheres, 0.645, is the largest among all the computed packing results for this packing assembly (Tables 1 and 2). In Figure 3, the η_{sph}^{rcp}(u, c_L) values of Table 3 pertaining to l/d = 0 (spheres) are included, divided by f_{sph}^{rcp}. One can also see that from c_L = 0 to c_L = 0.4 the generated packing fractions are in line with all other packing data: the computer-generated packing fractions [49-51], and Eqs. (23) and (34), respectively. Beyond c_L = 0.4, the protocol used in [53] starts to underpredict all other binary packing fractions, which are all consistent with each other. To quantify this anomaly, in Table 4, the ratio of η_{sph}^{rcp}(u, c_L) from Eqs. (23) and (34) and η_{sph}^{rcp}(u, c_L) from Table 3 (l/d = 0) are listed.
Indeed, the ratio is close to unity up to $c_L = 0.4$, and then the discrepancy rapidly increases with larger $c_L$, reaching a maximum relative difference that is close to 2% (1.019), reflecting the drop in packing fraction featured in [53] that can be clearly seen in Figure 3. Towards $c_L = 1$, the ratio tends to unity again.

| $c_L$ | $A$   |
|------|-------|
| 0.0  | 1.000 |
| 0.1  | 0.988 |
| 0.2  | 0.988 |
| 0.3  | 1.001 |
| 0.4  | 1.004 |
| 0.5  | 1.007 |
| 0.55 | 1.008 |
| 0.6  | 1.009 |
| 0.65 | 1.011 |
| 0.7  | 1.014 |
| 0.8  | 1.019 |
| 0.9  | 1.018 |
| 1.0  | 1.000 |

Table 4 RCP packing fraction $\eta_{spe}^{RCP}(u, c_L)$ following from Eqs. (23) and (34), divided by packing faction $\eta_{spe}^{RCP}(u, c_L)$ from spheres as simulated in [53], taken from Table 3 ($l/d = 0, f_{spe}^{RCP} = 0.645$).

In Figure 4a, the scaled binary packing fractions, as presented in [53], are set out for spherocylinders with $l/d = 0.1, 0.35, 1, 1.5, \text{and } 2$ (Table 3), as well as Eqs. (23) and (34), respectively. As expected, $f_{spe}^{RCP}$ depends on $l/d$. Furthermore, as with the spheres (Figure 3), the agreement between the simulations and model (Eqs. (23) and (34)) is very good for $c_L$ up to approximately 0.4. For a larger $c_L$ we see the same trend as for spheres; simulated packing fractions that drop and become smaller than might be expected. Accordingly, to compensate for this apparent simulation protocol anomaly, in Figure 4b, the data from Table 3 are included again but now multiplied (calibrated) with the ratios from Table 4, which are based on the experiment- and theory-based expressions (viz. Eqs. (23) and (34)), which were independently confirmed using three different simulation protocols (see Figure 3).
Figure 4 Bidisperse packing fraction, $\eta_{spc}(u, c_L)$, of randomly close packed binary spherocylinders with size ratio $u = 2$, and aspect ratios $l/d = 0.1, 0.35, 1, 1.5$ and $2$, as a function of the large sphere volume fraction $c_L$. a) Eqs. (23) and (34), and computer-generated data extracted from “Fig. 10” [53] (listed in Table 3). b) Eqs. (23) and (34), and the same computer-generated data from [53] (listed in Table 3), multiplied by the sphere-based adjustment $A$ as listed in Table 4.
Figure 4b reveals that when the data of [53] for spherocylinders with $l/d \neq 0$ is adjusted with the ratio obtained from sphere ($l/d = 0$) packing analysis, the agreement between the simulated packing and model becomes very good. Graphically, the difference between the model line and some of the data points may seem large; the difference is of order 1% or so.

4.3 Random loose packing

The equations based on Onsager’s theory revealed that the fitting coefficient $C$ from Mangelsdorf and Washington (Eq. (29)) includes the factor $(1 - f_{\text{spe}}^{\text{rcp}})$. The Mangelsdorf and Washington expression proved to be very accurate in the entire composition range, $0 \leq c_L \leq 1$, and size ratios $u$ up to 2 or so for binary RCP of spheres (Figure 3). This expression was therefore generalized to packings with different monosized packing fractions (Eqs. (23) and (34)), such as spherocylinders, and was validated in the previous subsection. Although the agreement was good (Figure 4), the monodisperse packing fractions $f_{\text{spe}}^{\text{rcp}}$ of all considered spherocylinders did not differ significantly from those of spheres (Table 3).

| $c_L$ | $u = 1.3$ | $u = 1.5$ | $u = 1.7$ | $u = 2$ |
|-------|-----------|-----------|-----------|--------|
| 0.0   | 0.5359    | 0.5359    | 0.5359    | 0.5359 |
| 0.1   | 0.5376    | 0.5393    | 0.5409    | 0.5429 |
| 0.2   | 0.5392    | 0.5426    | 0.5457    | 0.5500 |
| 0.3   | 0.5405    | 0.5456    | 0.5506    | 0.5571 |
| 0.4   | 0.5416    | 0.5482    | 0.5550    | 0.5641 |
| 0.5   | 0.5423    | 0.5503    | 0.5588    | 0.5707 |
| 0.6   | **0.5426**| 0.5516    | 0.5616    | 0.5764 |
| 0.7   | 0.5423    | **0.5517**| **0.5628**| **0.5803**|
| 0.8   | 0.5413    | 0.5499    | 0.5611    | 0.5802 |
| 0.9   | 0.5393    | 0.5453    | 0.5541    | 0.5711 |
| 1.0   | 0.5359    | 0.5359    | 0.5359    | 0.5359 |

Table 5 Binary packing fraction $\eta_{\text{spe}}^{\text{rlp}}(u, c_L)$ following from computer simulation of RLP of spheres with 4 different size ratios $u$ [51]. The maximum packing values $\eta_{\text{spe, max}}^{\text{rlp}}$ are indicated in bold.

Accordingly, in this subsection, Eqs. (23) and (34) are applied to the binary random loose packing (RLP) of the spheres. This packing arrangement has a monodisperse packing fraction which is very distinct from RCP, with $f_{\text{spe}}^{\text{rlp}} \approx 0.54$ as a generally accepted value for this lower limit of random sphere packing [6, 13, 20, 24-29, 51]. The magnitude of $(1 - f)$, as a factor introduced in Eq. (23), is therefore about 0.36 and 0.46 for RCP and RLP, respectively, and this difference is relatively even larger than their difference in $f$, viz. 0.64 and 0.54, respectively.
In Figure 5, the packing simulation results from the RLP of the spheres generated by [20, 51] are presented, which are listed in Table 5. In this figure, Eqs. (23) and (34) were included using \( f_{\text{spe}}^{\text{rlp}} = 0.536 \), taken from Table 5.

Figure 5 confirms that Eqs. (23) and (34) can accurately predict the binary RLP packing fraction of spheres in the entire compositional range \( 0 \leq c_L \leq 1 \) and for the size ratio range \( 1 \leq u \leq 2 \). This implies that Eqs. (23) and (34) are not only applicable to RCP, but also to RLP.

Based on the results shown in Figures 3-5, and the information provided by applying Onsager’s excluded volume model, it can be tentatively concluded that Eq. (21) (or Eq. (23)) and Eq. (34) are applicable to the loosest and densest packing states (RLP and RCP, respectively), and probably also for all intermediate states of compaction. It also seems applicable to spherocylinders with variable l/d, and probably to other particle shapes as well, although there is no rigorous proof yet for this claim. What is particularly remarkable is that the present model is based solely on analytical analysis (without introducing a fitting parameter). The only parameter, the monosized packing fraction, \( f \), is physically defined and is a function of only the considered particle shape and mode of packing (e.g. loose, close). In Section 6 the monodisperse packing fraction and the effect of compaction is analyzed in more detail. In the next section,
the difference in contraction functions $v(u)$, such as provided by the Onsager model, the Mangelsdorf and Washington model, and by [33], Eqs. (22), (34) and (35), respectively, is further analyzed.
5. Analysis of models

As seen before, for \( u \to 1 \), the Onsager- and Mangelsdorf- and Washington-based expressions coincide as Eqs. (22) and (34) coincide, as demonstrated in Subsection 3.2 and shown in Figure 2. On the other hand, for larger size differences (\( u \) deviating more from unity), the volume contraction functions begin to diverge. This contraction function governs the 3rd term in the denominator of Eqs. (21) and (23). The resulting difference in the predicted binary packing fraction is analyzed in more detail.

To characterize the effect of the different \( v(u) \) on the binary packing fraction \( \eta(u, X_L) \), the maximum packing fraction according to both approaches, being a function of the size ratio \( u \) only, is determined. For a given \( u \), the extremum in Eq. (21) follows from the partial derivative of \( \eta(u, X_L) \), with respect to \( X_L \):

\[
\eta_{X_L}(u, X_L) = \frac{\delta(X_L - 1)^2 + X_L^3 v(u)}{(X_L(\delta - 1) + 1 - \delta X_L(1 - X_L)v(u))^2}.
\]

Equating Eqs. (37) to zero yields the number fraction \( X_{L,max} \) and volume fraction \( c_{L,max} \), which results in the maximum packing for a given size ratio \( u \):

\[
X_{L,max} = \frac{1}{u^{3/2} + 1}; \quad c_{L,max} = \frac{u^{3/2}}{u^{3/2} + 1}.
\]

where \( c_{L,max} \) is obtained using Eq. (24), but it also follows from Eq. (23) and solving the \( \eta_{c_L}(u, c_L) = 0 \) problem. Note that these specific \( X_L \) and \( c_L \) values do not depend on \( v(u) \) nor on the monosized packing fraction \( f \). Eq. (38) also reveals that for \( u > 1 \), the maximum packing fraction is found for \( X_{L,max} < 0.5 \), and \( c_{L,max} > 0.5 \).

Figures 3-5 indeed show that the packing fraction is maximum for the larger particle volume fraction \( c_L \) exceeding parity, and that the eccentricity in the optimal packing composition increases with increasing \( u \), as predicted by Eq. (38). It is also interesting to note that \( X_{L,max} + c_{L,max} = 1 \), and hence, \( X_{L,max} \) and \( c_{L,max} \) are symmetrical with respect to 0.5 for all \( u \). In Figure 6, they are both set out against \( u \).

The composition corresponding to the maximum particle packing is a function of \( u \) only, and the corresponding maximum packing follows by substituting \( X_{L,max} \) from Eq. (38) into Eq. (21), or \( c_{L,max} \) from Eq. (38) into Eq. (23), and both yield
\[ \frac{\eta_{\text{max}} - f}{\eta_{\text{max}} (1 - f)} = \frac{v(u)}{(u^{3/2} + 1)^2}. \] (39)

This scaled maximum of the binary packing fraction does not depend on the monosized packing fraction \( f \) of the considered particle and contains the factor \((\eta_{\text{max}} - f)\), which is the packing increase due to binary polydispersity. One can also identify \((1 - f)\), which is the factor that follows the analysis of Onsager’s equations.

![Figure 6](image.png)

**Figure 6** Volume \( (c_{L,\text{max}}) \) and number \( (X_{L,\text{max}}) \) fraction, Eq. (38) of the large spheres, that result in a maximum packing fraction for bidisperse particle mixes, as a function of the size ratio \( u \). Both functions are symmetrical with respect to the horizontal line with value 0.5.

To illustrate the effect of \( v(u) \) given by Eqs. (22), (34), and (35), the resulting \((\eta_{\text{max}} - f)/\eta_{\text{max}}(1 - f)\) values are shown in Figure 7. The difference in the packing maximum predicted by the Onsager- and Mangelsdorf and Washington-based models for a given \( u \) is very minor for a small \( u - 1 \), which is not surprising, as both Eqs. (22) and (34) tend to \(2(u - 1)^2\) for \( u \to 1 \). However, for a larger \( u \), the difference becomes more pronounced, and at \( u = 2 \), it is approximately 25\%, which is also seen in Figure 2. Figure 7 also shows the linear approximation of the contraction function (Eq. (35)) is close to the second-order models based on the Onsager model and Mangelsdorf and Washington experiments, but is less accurate in the entire range of \(1 \leq u \leq 2\). For a small \( u - 1 \), owing to its linear dependence on \( u - 1 \), it
overestimates the packing fraction, whereas for \( u \to 2 \) and larger, it underestimates the binary packing fraction.

**Figure 7** Scaled highest packing fraction, \( (\eta_{\text{max}} - f)/\eta_{\text{max}}(1 - f) \), as a function of the size ratio \( u \), \( u \) ranging from unity to two, computed with Eq. (39) and using Eqs. (22), (34) and (35), for the latter \( \beta = 0.20 \) is employed [33, 48]. In this figure also the scaled maximum packing fractions extracted from Tables 1 and 3 are included.

Figures 3-5 showed that Eqs. (23) and (34) capture the binary packing fraction very well over the entire considered size ratio range of \( 1 \leq u \leq 2 \). That Eq. (23) with Eq. (34) best captures the binary packing fraction is also confirmed by the scaled packing maxima that follow from the packing simulations (taken from Tables 1 and 5), which are included in Figure 7. The figure also shows that the scaled RLP packing maxima coincide with RCP values. This conclusion is not obvious, and once more emphasizes the importance of the scaling factor \((1 - f)\) that followed from comparing the Onsager- and Mangelsdorf and Washington-based models (Section 3). The agreement of the different simulation protocols illustrates that the packing fractions as such may differ (Table 1), but that \( (\eta_{\text{max}} - f)/\eta_{\text{max}}(1 - f) \) are very similar. In other words, though the computed monosized and bidisperse packing fractions differ, the maximum effect of bidisperse polydispersity on packing fraction, governed by \((\eta_{\text{max}} - f)/\eta_{\text{max}}(1 - f)\), is almost identical.
6. Packing fraction of monodisperse particles

In Sections 3 it was seen that the Onsager-based model predicts a packing increase by bidispersity that amounts to \( 2f(1-f)X_1(1-X_1)(u-1)^2 + O((u-1)^3) \), Eq. (31). The monodisperse packing fraction \( f \) depends on particle shape and its densification (the Appendix for instance addresses the monodisperse packing fraction of (sphero)cylinders with different l/d, that is different shapes). Monodisperse particles can be packed between the loosest and closest states of densification, the packing fraction being \( f_{rlp} \leq f \leq f_{rcp} \). This implies that the factor \( 2f(1-f) \) depends on the packing configuration. In this section, the range of \( f \) is investigated, as well as a map of known \( f_{rlp} \) and \( f_{rcp} \) combinations for a number of particle shapes is introduced.

6.1 Packing fraction range of a particle shape

The packing fraction of particle may range from its loosest possible state of packing (RLP), to its densest state of packing (RCP). Figure 8 depicts combinations of \( (f_{rlp}, f_{rcp}) \) for a number of particle shapes, taken from literature. For spheres the point \( (f_{rlp}^{spe} = 0.54, f_{rcp}^{spe} = 0.64) \) is included. In Table 7 the RLP and RCP void fractions of the five platonic solids, taken from [54], are listed, and included in Figure 8 as well. These authors experimentally determined the RLP and RCP packing fractions of the monodisperse five platonic solids: tetrahedron, cube, octahedron, dodecahedron, and icosahedron, all having slightly rounded edges.

| Shape      | \( f_{rlp} \) | \( f_{rcp} \) |
|------------|---------------|---------------|
| Tetrahedron| 0.36          | 0.49          |
| Cube       | 0.33          | 0.46          |
| Octahedron | 0.36          | 0.48          |
| Dodecahedron| 0.37         | 0.49          |
| Icosahedron| 0.41          | 0.50          |

Table 7 Random loose and close packing fractions of five platonic solids as measured by [54].

Furthermore, for a number of disks (\( l/d < 1 \)), equilateral cylinders (\( l/d = 1 \)) and cylinders (\( l/d > 1 \)), and other-shaped particles, the RLP and RCP void fractions were measured by [55], depicted in their “Fig. 2a” and “Fig. 2b”, respectively, versus the Wadell sphericity. The disks’ l/d is taken from “Table 1”, and the cylinders’ l/d from the main text [55]. From this these l/d the Wadell sphericity is computed (Table 8), which match excellently with the Wadell sphericity from “Fig. 2” [55]. Hence, for each particle, \( f_{rlp} \) and \( f_{rcp} \) can be derived from their “Fig. 2a”
and “Fig. 2b” [55], respectively, which are summarized in Table 8, and they are included in Figure 8 as well.

| Cylinders | Disks | Other-shaped particles |
|-----------|-------|------------------------|
| Ψ | l/d | \(f_{rlp}^{cyl}\) | \(f_{rcp}^{cyl}\) | Ψ | l/d | \(f_{rlp}^{cyl}\) | \(f_{rcp}^{cyl}\) | Ψ | \(f_{rlp}\) | \(f_{rcp}\) |
| 0.874 | 1 | 0.590 | 0.702 | 0.594 | 0.1656 | 0.563 | 0.671 | 0.862 | 0.613 | 0.644 |
| 0.734 | 4 | 0.534 | 0.636 | 0.520 | 0.1229 | 0.553 | 0.635 | 0.821 | 0.598 | 0.671 |
| 0.677 | 5.6 | 0.481 | 0.610 | 0.352 | 0.0579 | 0.418 | 0.558 | 0.801 | 0.604 | 0.658 |
| 0.617 | 8 | 0.463 | 0.582 | 0.200 | 0.0225 | 0.361 | 0.469 | 0.793 | 0.588 | 0.671 |
| 0.561 | 11.2 | 0.428 | 0.515 | 0.169 | 0.0172 | 0.307 | 0.433 | 0.769 | 0.570 | 0.624 |
| 0.504 | 16 | 0.310 | 0.436 | 0.133 | 0.0119 | 0.285 | 0.403 | 0.737 | 0.566 | 0.645 |
| 0.455 | 22.4 | 0.269 | 0.345 | 0.094 | 0.0094 | 0.270 | 0.384 | 0.723 | 0.564 | 0.645 |
| 0.406 | 32 | 0.171 | 0.234 | | | | | 0.684 | 0.567 | 0.655 |
| 0.365 | 44.8 | 0.101 | 0.142 | | | | | 0.568 | 0.504 | 0.596 |
| 0.325 | 64 | 0.063 | 0.097 | | | | | 0.554 | 0.574 | 0.651 |

Table 8 Measured RCP and RLP packing fraction values for different particle shapes and their pertaining l/d (\(\alpha^1\)) and Wadell sphericity Ψ values, derived from “Fig. 2” of [55]. The disks’ l/d is taken from “Table 1”, and the cylinders’ l/d from the main text [55]. For cylinders and disks, Ψ = 2 (3/2)\(^{2/3}\) \(\alpha^{1/3}/(2 + \alpha)\).

One can see in Figure 8 that for all particles \(f_{rcp} > f_{rlp}\), as would be expected, so all \((f_{rlp}, f_{rcp})\) are located above the diagonal \(f_{rcp} = f_{rlp}\) (parity line in Figure 8). From basic principles it is required that \(f_{rlp}\) and \(f_{rcp}\) coincide when \(f_{rcp}\) and \(f_{rlp}\) approach zero and unity, respectively, since \(0 \leq f_{rlp} < f_{rcp} \leq 1\). One can observe that the difference between \(f_{rcp}\) and \(f_{rcp}\) diminishes when they tend to zero and unity indeed. It also appears that all combinations of \(f_{rlp}\) and \(f_{rcp}\) are located below a curve that obeys \((f_{rlp} = 0, f_{rcp} = 0)\) and \((f_{rlp} = 1, f_{rcp} = 1)\). Hence, it is plausible to propose as ansatz an upper bound to the random close packing value, depending on the random loose packing value, as

\[
f_{rcp} = f_{rlp} + B f_{rlp} (1 - f_{rlp}),
\]

with \(B > 0\), which is a parabola superimposed on the line \(f_{rcp} = f_{rlp}\). The equation furthermore fulfills the conditions \(f_{rcp} > f_{rlp}\), \(f_{rlp} = f_{rcp} = 0\), and \(f_{rlp} = f_{rcp} = 1\), and hence has the good
The inverse relation, \( f_{rlp} \) for a given \( f_{rcp} \) follows from solving Eq. (37), yielding:

\[
f_{rlp} = \frac{1 + B - \sqrt{(B + 1)^2 - 4Bf_{rcp}}}{2B}.
\]  

(38)

Also this expression, obviously, fulfils the conditions \( f_{rlp} \leq f_{rcp} \), \( f_{rcp} = f_{rlp} = 0 \), and \( f_{rcp} = f_{rlp} = 1 \). It appears that all \((f_{rlp}, f_{rcp})\) values are below Eq. (37) for \( B \approx 0.6 \), which is a putative maximum (Figure 8).

Figure 8: Packing fraction map of monosized particles close packing fraction \( f_{rcp} \) as a function of their loose packing fraction \( f_{rlp} \) (shaded area). The curve pertaining to the maximum packing fraction, \( f_{rcp} \), is shown using Eq. (37) with \( B = 0.6 \), as well as measured combinations of \( f_{rlp} \) and \( f_{rcp} \) values for a number of particle shapes, taken from Tables 7 and 8. For spheres as \((f_{spe}_{rlp}, f_{spe}_{rcp})\) values \((0.54, 0.64)\) and \((0.49, 0.64)\) are included. The fitted cylinder packing fractions \((0 \leq l/d < \infty)\), Eq. (A.11) for RLP and RCP, is included as well.

The factor \( B \) characterizes the curvature of the upper threshold. Eq. (37) with \( B = 0.6 \) is included in Figure 8, and one can see that indeed almost all combinations of \((f_{rlp}, f_{rcp})\) are located in the area (shaded) enclosed by line \( f_{rcp} = f_{rlp} \) and Eq. (37). Many points are located on the curve, notwithstanding that the packing fraction of different particle shapes, but with identical \( \Psi \), may differ (see “Fig. 2” [55] and Table 8), many \( f_{rcp} \) and \( f_{rlp} \) seem to obey Eq. (37).
Many combinations of \((f_{\text{rlp}}, f_{\text{rcp}})\) are located within the shaded area. It is conceivable, though still rather speculative, to believe that for these particles, in order to have \((f_{\text{rlp}}, f_{\text{rcp}})\) located on the threshold line, either the true RLP or RCP packing configuration, or both, of such particle were not measured or computed. There is no proof for this conjecture, but if the actual \(f_{\text{rcp}}\) of such particle would be higher, a data point moves upward, and if the actual \(f_{\text{rlp}}\) would be lower, it moves to the left. In both cases the threshold curve is then approached.

In this respect, a nice example is \((f_{\text{spe}, \text{rlp}}, f_{\text{spe, rcp}})\) of spheres. The depicted combination of \((0.54, 0.64)\), is located within the area, and not on the proposed boundary, Eq. (37). The RCP fraction of spheres is undisputedly close to this value of 0.64, but the value for RLP is less agreed upon. To be located on Eq. (37), the required \(f_{\text{rlp}}\) follows from Eq. (38) by substituting \(f_{\text{spe, rcp}} = 0.64\) and \(B = 0.6\), yielding \(f_{\text{spe, rlp}} = 0.49\). Interestingly, in [23] a RLP packing fraction lower than 0.54 was proposed indeed, namely a lowest packing fraction of 0.49 for strictly jammed frictionless spheres, a value that would render \((f_{\text{spe, rlp}}, f_{\text{spe, rcp}})\) of spheres being located on the boundary curve. This second spheres point \((f_{\text{spe, rlp}}, f_{\text{spe, rcp}}) = (0.49, 0.64)\) is therefore added to Figure 8 as well.

In Figure 8, also the RCP and RLP packing fractions of cylinders for \(0 \leq l/d \leq 180\), based on Eq. (A.11), is included as well. For these \(l/d\), the packing fraction \((f_{\text{cyl, rlp}}, f_{\text{cyl, rcp}})\) range from \((0, 0)\) to maxima \((0.58, 0.72)\), see Appendix. The former combination is attained for \(l/d = 0\) \((\alpha^{-1})\), the maximum at \(l/d = 0.384\) \((\alpha_{\text{max}} = 2.6)\). Figure 8 reveals that the combination of fitted RLP and RCP packing fractions follows the threshold curve Eq. (37) very closely for all \(l/d\), whereby each \(l/d\) \((or \alpha)\) represents a distinct particle shape.

### 6.2 Effect of packing configuration on bidisperse packing

Based on putative threshold Eq. (37), it is possible to assess the range of \(f(1-f)\), that is a factor in the bidisperse packing increase (e.g. Eqs. (31) and (36)), for \(f\) ranging from \(f_{\text{rlp}}\) to \(f_{\text{rcp}}\), so the applicable packing configuration. Using Eq. (37), it follows that

\[
f_{\text{cp}}(1 - f_{\text{rcp}}) = f_{\text{rlp}}(1 - f_{\text{rlp}})(1 - Bf_{\text{rlp}})(1 + B - Bf_{\text{rlp}}),
\]

(39)

As \(f_{\text{rlp}} \leq f \leq f_{\text{rcp}}\), now also the effect of densification on the range of \(f(1-f)\) values can be quantified. Eq. (39) reveals that the RCP/RLP ratio of the product \(f(1-f)\) is \((1 - Bf_{\text{rlp}})(1 + B - Bf_{\text{rlp}})\). By differentiation it readily follows that this function is decreasing from \(f_{\text{rlp}} = 0\) to \(f_{\text{rlp}} = 1\), at \(f_{\text{rlp}} = 0\) it is 1.6, and at \(f_{\text{rlp}} = 1\), \((1 - Bf_{\text{rlp}})(1 + B - Bf_{\text{rlp}}) = 0.4\). Hence, for particles with larger \(f_{\text{rlp}}\) (and larger \(f_{\text{rcp}}\), a denser configuration will result in a
higher \( f(1 - f) \). In other words, the effect of bidisperse packing increase will then be more pronounced. On the other hand, for particles with small \( f_{rlp} \), e.g. (spherocylinders with high aspect ratio \( l/d \) (see Appendix), loose packings will have a higher \( f(1 - f) \) than their denser configuration.

Now the question arises whether the packing fraction of a bidisperse close packing always exceeds that of the loose bidisperse particle packing, both having the same composition and size ratio. In that case:

\[
\begin{align*}
\frac{f_{rcp}}{f_{rlp}} + 2\frac{f_{rcp}}{2f_{rcp}}(1 - f_{rcp})X_L(1 - X_L)(u - 1)^2 > \frac{f_{rlp}}{f_{rlp}} + 2\frac{f_{rlp}}{f_{rlp}}X_L(1 - X_L)(u - 1)^2 .
\end{align*}
\]

(40)

Substituting Eqs. (37) and (39) yields the requirement

\[
\begin{align*}
B + 2(1 - Br_{rlp})(1 + B - Br_{rlp})X_L(1 - X_L)(u - 1)^2 > 2X_L(1 - X_L)(u - 1)^2 .
\end{align*}
\]

(41)

As \((u - 1)^2 \leq 1\), \(X_L(1 - X_L) \leq \frac{1}{4}\), and \(B = 0.6\), Eq. (41), and consequently Eq. (40) as well, is always fulfilled. Hence, for each particle type and \( u \leq 2 \), bidispersity cannot render its RLP packing fraction exceed its RCP packing fraction.
7. Concluding remarks

In this study, the packing fraction of polydisperse packings was addressed, in particular, the packing of binary assemblies with a limited size ratio $u$ (maximum 2 to 2.5 or so), obtained by combining two uniformly shaped (similar) particles of different sizes. Here, the packing of random bidisperse particles with small size differences is studied in detail by revisiting Onsager’s theory, which is based on excluded volume and was originally developed to model the liquid-to-nematic (I-N) phase transition of hard rod-like (spherocylinders and cylinders) particles [1].

The Onsager expressions for the excluded volume have so far only been used to study the packing of identical particles, although his theory allows for two (sphero)cylinders with different diameters and lengths. In this study, it is applied to the packing of bidisperse similar (sphero)cylinders, i.e. with the same aspect (length/diameter) ratio $\alpha (=d/l)$.

Using a statistical approach, in Section 2, binary Onsager expressions are used to derive a closed-form expression for the excluded volume, and subsequently, the binary packing fraction of the aforesaid particles. It appears that the expressions for spherocylinders and cylinders are identical (Eqs. (21) and (23)), irrespective of the aspect ratio. From a Taylor expansion, it follows that the bidisperse variation from the monosized packing fraction amounts to $2f(1 – f)X_1(1 – X_1)(u – 1)^2 + O((u – 1)^3); \text{ hence, is a function of the concentration } X_1 \text{ and proportional to the square of the relative size difference } u – 1$. In Section 3, a bidisperse packing fraction expression is derived based on a semi-empirical model of the RCP of spheres [2]. It is shown that for $u \to 1$, this semi-empirical expression coincides with the expression obtained from using Onsager’s model, which is also applicable to spheres. It furthermore appears that the fitting parameter $C$ [2] is uniquely related to $(1 – f)$.

To validate and compare the obtained expressions for the packing increase, in Section 4, they are first compared with numerical simulations of binary RCP of spheres [49-51] over the entire compositional range (concentration from zero to unity) and for size ratios $u$ up to well over two [52]. For a size ratio $u$ value towards 2, Eq. (34), following [2], is more accurate than Eq. (22) following Onsager’s model [1], resulting in Eqs. (21) and (23) in combination with Eq. (34) as a general bidisperse packing fraction applicable to $u$ up to 2–2.5. Subsequently, a comparison with RCP for spherocylinders with l/d ranging from 0.1 to 2, and $u = 2$, yields again good agreement. Finally, the general packing expression is applied to and compared with the computationally generated RLP of spheres [51], for which the factor $(1 – f)$ is 25% larger than...
for RCP, and excellent agreement is found in the entire compositional range and for size ratios 
v up to 2.

In Section 5, the different approaches to the binary packing fraction are mutually compared by computing their scaled maximum packing fraction, which no longer depends on monodisperse packing fraction \( f \), but on the size ratio \( u \) only. In Figure 7, the scaled maximum packing fractions of these models, which have different contraction functions \( v(u) \), are set out, as well as the corresponding results of the computer simulations (both RCP and RLP of spheres), again confirming that the combination of Eq. (21) (or Eq. (23)) and Eq. (34) yield the most accurate results.

In Section 6, the magnitude of the factor \( f(1 - f) \), governing the bidisperse packing increase, of a particle shape is assessed by considering its packing fraction range, that may range from \( f_{rlp} \) to \( f_{rcp} \). First a packing fraction map is introduced (Figure 8), that covers the area of known possible combinations of \( f_{rlp} \) and \( f_{rcp} \) from a number of particle shapes. An explicit threshold (Eq. (37)) is proposed, and subsequently the effect of the packing configuration on the factor \( f(1 - f) \) clarified. Eq. (37), with \( B = 0.6 \), appears to be an upper threshold of \( (f_{rlp}, f_{rcp}) \) combinations that of measured monodisperse loose and close packing data of many different particle shapes, and many \( (f_{rlp}, f_{rcp}) \) combinations are located on the threshold (Figure 8).

The Appendix contains a literature review of monodisperse (sphero)cylinder packing data, RLP and RCP. It appears that the monodisperse packing expressions following from Onsager’s excluded volume, Eqs. (6) and (7), are in qualitative agreement. This is not a surprise as Onsager’s theory was not developed for assessing the packing fraction of monosized RCP nor RLP packings. Notwithstanding this conclusion for the monodisperse situation, this paper reveals that the excluded volume approach yields a quantitative correct expression for the bidisperse case.

As stated in the Introduction, for binary mixes with size ratio \( u \to \infty \), i.e. two noninteracting size classes, an analytical expression for the binary void fraction is available \([18, 35, 36]\). Revisiting and applying Onsager’s model to binary particle packings yields a generic and accurate packing expression applicable to the opposite limit: size ratios \( u \) from unity to at least two, applicable to RLP and RCP (and probably also other intermediate states of packing), to (sphero)cylinders with all \( \alpha \), and probably many more particle shapes as well. This parameter-free closed-form expression is entirely characterized by the concentration (either number fraction \( X_L \), Eq. (21) or volume fraction \( c_L \), Eq. (23)) of the two components, particle size ratio \( u \), and monosized packing fraction \( f \). For the contraction function \( v(u) \), Eq. (34), based on [2], is appropriate.
Finally, it is noteworthy that the derived generic model is based solely on physical principles, and no adjustable parameters have been introduced to obtain the presented results. The governing parameters, *i.e.* the monosized packing fraction $f$, size ratio $u$, and concentration ($X_L$ or $c_L$), are all physically defined. For instance, the monosized packing fraction depends only on the considered particle shape (*e.g.* cylinder, spherocylinder, and sphere) and the state of packing densification (*e.g.* loose, close).
Appendix

In this appendix the packing fraction following from the excluded volume approach of Onsager [1] is compared with monodisperse packing data from literature. The limiting behaviour ($\alpha \downarrow 0$ and $\alpha \to \infty$), and the extrema of the monosized packing expressions for spherocylinders and cylinders, are examined.

A.1 Spherocylinders and cylinders, large l/d

For long spherocylinders and cylinders (having no end caps), one finds the same asymptotic relation because for large l/d ($\alpha \downarrow 0$), the detailed shape of their ends is irrelevant. Furthermore, for small $\alpha$ (large l/d), random close and loose packing values both tend to zero (Section 6). First, reported packing values in this limit are presented.

Philipse [46] proposed a random contact model and related the number of contacts per particle and excluded volume to the packing fraction of (sphero)cylinders with a large aspect ratio l/d, and argued the packing fraction is proportional to the aspect ratio $\alpha$ (d/l). The number of contacts is probably the second most investigated property in studying a particle packing, as it is a basic topological parameter that provides insight into packing configurations and their stability. Based on the contact model, the packing fraction of both cylinders and spherocylinders is asymptotically approximated by [46]:

$$f = z\alpha(1 + O(\alpha)),$$  \hspace{1cm} (A.1)

and fitted $z = 5.4 \pm 0.2$ to packing data. This $\alpha$ dependence also follows from Eqs. (6) and (7) for small $\alpha$. This equation is very similar to the equation (“Eq. (68)”, rewritten here) introduced earlier by Pan [11]:

$$f = z\alpha \left(1 - \frac{z\pi\alpha}{2}\right)^{-1} = z\alpha(1 + O(\alpha)),$$ \hspace{1cm} (A.2)

Blouwolff and Faden [56] counted the mean number of contacts per particle $Z$, i.e. the coordination number, in experimental random thin-rod packings and confirmed that $Z$ is approximately 10 ($Z = 2z$) for long cylinders. In addition, they erroneously used the factor $(2\pi + 3)/4$ in Eq. (4), instead of the correct $(\pi + 3)/4$. This packing law, Eqs. (A.1)–(A.2), has been
confirmed by experiments [9, 10, 57] as well as by simulations [58], yielding \( z \) in the range of 5.1-5.5.

**A.2 Spherocylinders, finite l/d**

Next, also larger \( d/l \) are considered, whereby the packing fraction spherocylinders and cylinders start deviating from each other. For spherocylinders, the packing fraction tends to a non-zero value, for \( l/d \) tending to zero (\( \alpha \to \infty \)), see Eq. (6), that is when the monosized packing of spheres is attained. This situation yields a packing fraction \( f_{\text{spe}} = \frac{1}{4} \), see Eq. (6), which does not match the established values of \( f_{\text{spe}}^{\text{rcp}} \) nor \( f_{\text{spe}}^{\text{rlp}} \). This case is depicted in Figure 1, in which 2 spheres, with a total volume of \( \pi d^3/3 \) and that have an excluded volume of \( 4\pi d^3/3 \), can be recognized. A maximum packing fraction is observed for a \( l/d \) (\( \alpha^{-1} \)) larger than zero [53, 58-60].

First, spherocylinders Eq. (6) is generalized to

\[
f_{\text{spe}}(\alpha) \approx z \left( \frac{\alpha + c_1 \alpha^2}{1 + c_2 \alpha + c_3 \alpha^2} \right) = z \left( \frac{\alpha^{-1} + c_1}{\alpha^{-2} + c_2 \alpha^{-1} + c_3} \right).
\] (A.3)

Note that for \( \alpha \downarrow 0 \), Eq. (A.1) is obtained. To the best of the author’s knowledge, only random close packing of spherocylinders has been reported in literature, and hence only this RCP configuration is addressed here.

| l/d | \( f_{\text{spe}}^{\text{rcp}} \) | l/d | \( f_{\text{spe}}^{\text{rcp}} \) | l/d | \( f_{\text{spe}}^{\text{rcp}} \) |
|-----|-----------------|-----|-----------------|-----|-----------------|
| 0   | 0.645           | 0.7 | 0.675           | 1.8 | 0.633           |
| 0.1 | 0.672           | 0.8 | 0.673           | 2   | 0.629           |
| 0.2 | 0.685           | 0.9 | 0.668           | 2.2 | 0.614           |
| 0.3 | 0.689           | 1   | 0.659           | 2.5 | 0.604           |
| 0.35| 0.686           | 1.2 | 0.656           | 3   | 0.576           |
| 0.4 | 0.687           | 1.4 | 0.650           | 3.5 | 0.558           |
| 0.5 | 0.684           | 1.5 | 0.643           | 4   | 0.536           |
| 0.6 | 0.679           | 1.6 | 0.642           |

**Table A.1** Computed RCP packing fraction values for spherocylinders for different \( l/d \) (\( \alpha^{-1} \)), taken from “Fig. 4” [53].

When the aspect ratio \( \alpha \to \infty \) (so \( l/d \downarrow 0 \)), the RCP fraction of monosized spheres is obtained, \( f_{\text{spe}}^{\text{rcp}} \), so Eq. (A.3) yields
From literature it is also known that a maximum packing fraction is obtained for $l/d \approx 0.3$-$0.5$, whereby $f_{\text{spc, rcp}}^{\text{max}} \approx 0.72$ \cite{59, 60}. In \cite{53, 59} a broad collection of published packing data on monosized spherocylinders for $l/d$ up to 6 are reviewed, which are consistent with this conclusion. Here, the computational data, extracted from \cite{53, 58} and listed in Tables A.1 and A.2, are set out in Figure A.1. One can see the RCP packing fraction that is attained at $\alpha^{-1} (= d/l) = 0$, a maximum packing fraction at $\alpha_{\text{max}} \approx 2.6$, and a packing fraction that tends to zero for $\alpha \downarrow 0 (l/d \to \infty)$, see previous subsection.

| $l/d$ | $f_{\text{spc, rcp}}$ |
|-------|------------------|
| 0     | 0.634            |
| 0.4   | 0.695            |
| 1     | 0.682            |
| 2     | 0.615            |
| 4     | 0.536            |
| 8     | 0.420            |
| 20    | 0.226            |
| 40    | 0.128            |
| 80    | 0.060            |
| 120   | 0.034            |
| 160   | 0.025            |

Table A.2 Computed RCP packing fraction values for spherocylinders for different $l/d (\alpha^{-1})$, derived from “Fig. 2” \cite{58}.

The aspect ratio $\alpha$ that yields this maximum packing fraction, $\alpha_{\text{max}}$, follows from differentiating the right-hand side of Eq. (A.3) with respect to $\alpha$ and equating the result to zero, yielding:

$$1 + 2\alpha_{\text{max}} + (c_1 c_2 - c_3) \alpha_{\text{max}}^2 = 0 ,$$

(A.5)

and the pertaining packing fraction is designated $f_{\text{spc, rcp}}^{\text{max}}$:

$$f_{\text{spc, rcp}}^{\text{max}} = z \left( \frac{\alpha_{\text{max}}^2 + c_1 \alpha_{\text{max}}^4}{1 + c_2 \alpha_{\text{max}}^2 + c_3 \alpha_{\text{max}}^4} \right) .$$

(A.6)

Combining Eqs. (A.4)-(A.6) now yields the following quadratic equation in $c_1$:  

$$c_3 = \frac{c_1 z}{r_{\text{spc}}^{\text{rcp}}} ,$$

(A.4)
\[ c_1^2 \left( \frac{r_{\text{spc, max}}^{\text{rcp}}}{r_{\text{spe}}^{\text{rcp}}} - 1 \right) \alpha_{\text{max}}^2 z + c_1 \left( \frac{r_{\text{spc, max}}^{\text{rcp}}}{r_{\text{spe}}^{\text{rcp}}} - 1 \right) \alpha_{\text{max}}^2 z - r_{\text{spc, max}}^{\text{rcp}} \alpha_{\text{max}} - r_{\text{spc, max}}^{\text{rcp}} = 0 , \] (A.7)

yielding

\[ c_1 = \frac{r_{\text{spc, max}}^{\text{rcp}}}{r_{\text{spc, max}}^{\text{rcp}} - r_{\text{spe}}^{\text{rcp}}} \alpha_{\text{max}}^2 z , \] (A.8)

\[ c_2 = \frac{z}{r_{\text{spc, max}}^{\text{rcp}}} - \frac{2}{\alpha_{\text{max}}} , \] (A.9)

and

\[ c_3 = \frac{r_{\text{spc, max}}^{\text{rcp}}}{r_{\text{spc, max}}^{\text{rcp}} - r_{\text{spe}}^{\text{rcp}}} \alpha_{\text{max}}^2 . \] (A.10)

With \( z = 5.3, r_{\text{spe}}^{\text{rcp}} = 0.64, \alpha_{\text{max}} = 2.6 \) (\(l/d = 0.385\)) and \( r_{\text{spc, max}}^{\text{rcp}} = 0.72\) \([59, 60]\), it follows that \(c_1 = 0.161, c_2 = 6.592\) and \(c_3 = 1.331\). Eq. (A.6), with these values, is set out in Figure A.1.

Figure A.1 Random close packing fraction of monosized spherocylinders \( r_{\text{spc}}^{\text{rcp}} \) as a function of the aspect ratio \( l/d \) \((\alpha^{-1})\) according to Eq. (A.6) with \( z = 5.3, c_1 = 0.161, c_2 = 6.592\) and \( c_3 = 1.331\). The computational data of \([53, 58]\) are included as well (Tables A.1 and A.2). The inset shows a magnified view of the same graph for small \(l/d\).
The figure shows a good agreement between the fitted Onsager-based model, Eq. (A.6), and the spherocylinder random close packing values reported in literature (Tables A.1 and A.2).

### A.3 Cylinders, finite l/d

In contrast to spherocylinders, Eq. (7) reveals that for cylinders the packing fraction tends to zero both for both d/l ($\alpha$) and l/d ($\alpha^{-1}$) tending to zero, with a maximum monosized packing fraction for l/d ($\alpha^{-1}$) larger than zero, similar as for spherocylinders.

| l/d | $f_{\text{rcp}}^{\text{cyl}}$ | l/d | $f_{\text{rcp}}^{\text{cyl}}$ |
|-----|-----------------|-----|-----------------|
| 0.86| 0.720           | 15.7| 0.312           |
| 1.7 | 0.636           | 16.2| 0.289           |
| 4.0 | 0.579           | 19.1| 0.255           |
| 6.9 | 0.491           | 24.8| 0.205           |
| 7.2 | 0.507           | 25.5| 0.195           |
| 8.1 | 0.391           | 37.4| 0.132           |
| 10.5| 0.416           | 49.3| 0.103           |
| 15.2| 0.266           | 51  | 0.105           |

Table A.3 Experimental RCP packing fraction values for cylinders for different l/d ($\alpha^{-1}$), taken from “Fig. 4” [8].

This trend has been observed in literature too [55]. For cylinders, both random loose and random close packing experiments are reported in literature.

First, Eq. (7) is generalized to

$$ f_{\text{cyl}}(\alpha) = z \left( \frac{\alpha}{1 + c_1 \alpha + c_2 \alpha^2} \right) = z \left( \frac{\alpha^{-1}}{\alpha^{-2} + c_1 \alpha^{-1} + c_2} \right). \quad (A.11) $$

| l/d | $f_{\text{rcp}}^{\text{cyl}}$ | l/d | $f_{\text{rcp}}^{\text{cyl}}$ |
|-----|-----------------|-----|-----------------|
| 0.53| 0.617           | 60  | 0.081           |
| 0.63| 0.613           | 90  | 0.050           |
| 1   | 0.629           | 34  | 0.197           |
| 1.2 | 0.607           | 49  | 0.080           |
| 1.3 | 0.585           | 59  | 0.070           |
| 11  | 0.403           | 60  | 0.087           |
| 15  | 0.300           | 90  | 0.056           |
| 34  | 0.145           | 167 | 0.033           |

Table A.4 Experimental RCP packing fraction values for cylinders for different l/d ($\alpha^{-1}$), taken from “Tableau 4” and “Tableau 5” [10].
Note that for $\alpha \downarrow 0$, Eq. (A.11) yields Eq. (A.1), and that for $\alpha \to \infty$ (so $l/d \downarrow 0$), this equation yields a packing fraction tending to zero as well. It appears that Eq. (A.11), with using the same $\alpha_{\text{max}}$ and $f_{cyl,\text{max}}^{rcp}$ as for spherocylinders, good agreement is obtained.

**Figure A.2** Random close packing fraction of monosized cylinders $f_{cyl}^{rcp}$ as a function of the aspect ratio $l/d$ ($\alpha^{-1}$) according to Eq. (A.11) with $z = 5.3$, $c_1 = 6.592$ and $c_2 = 0.148$. The experimental data of [8, 10, 55] are included as well (Tables 8, A.3 and A.4). The inset shows a magnified view of the same graph for small $l/d$. The aspect ratio $\alpha$ that yields the maximum packing fraction, $\alpha_{\text{max}}$, follows from differentiating the right-hand side with respect to $\alpha$ and equating the result to zero, yielding:

$$c_1 = \frac{z}{f_{cyl,\text{max}}^{rcp}} - \frac{2}{\alpha_{\text{max}}} , \quad (A.12)$$

and the pertaining packing fraction is designated $f_{cyl,\text{max}}^{rcp}$. Eqs. (A.11) and (A.12) yielding

$$c_2 = \frac{1}{\alpha_{\text{max}}^2} . \quad (A.13)$$

In Figure A.2 measured random close packing data for cylinders and disks are included [8, 10, 55], listed in Tables 8, A.3 and A.4. Onsager-based Eq. (A.11) is fitted using $z = 5.3$, $\alpha_{\text{max}} = 2.6$ and $f_{cyl,\text{max}}^{rcp} = 0.72$, it follows that $c_1 = 6.592$ and $c_2 = 0.148$. 

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Table A.5 Experimental RLP packing fraction values for cylinders for different l/d (α⁻¹), taken from “Tableau 5” [10].

In Figure A.3, measured random loose packing data for cylinders and disks are included [10, 55], listed in Tables 8 and A.5. Onsager-based Eq. (A.11) is fitted using z = 3.3, αmax = 2.6 and \( f_{cyl,\text{rlp}} \) = 0.58, it follows that c₁ = 4.920 and c₂ = 0.148.

![Figure A.3](image)

Figure A.3 Random loose packing fraction of monosized cylinders \( f_{cyl,\text{rlp}} \) as a function of the aspect ratio l/d (α⁻¹) according to Eq. (A.11) with z = 3.3, c₁ = 4.920 and c₂ = 0.148. The experimental data of [10, 55] are included as well (Tables 8 and A.5). The inset shows a magnified view of the same graph for small l/d.

Also here we see that the Onsager-based model captures the packing fractions quite well, in the entire α (or l/d) range.
In this Appendix, modified Onsager-based equations have been applied to RCP of (sphero)cylinders and RLP of cylinders, based on a thorough study of reported computational and experimental data. This yields the important conclusion that for all three monodisperse assemblies the maximum packing seems to take place for aspect ratio $\alpha_{\text{max}} \approx 2.6$ ($l/d \approx 0.38$). Furthermore, the maximum RCP packing fraction of spherocylinders and cylinders seems to be very similar, $f_{\text{spc,max}}^{\text{rcp}} \approx f_{\text{cyl,max}}^{\text{rcp}} \approx 0.72$. Also for large $l/d$, spherocylinders and cylinders feature the same packing fraction.
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