Beiträge zur Algebra und Geometrie
Contributions to Algebra and Geometry
Volume 51 (2010), No. 2, 337-344.

Dense Binary Sphere Packings

Gavin W. Marshall **Toby S. Hudson**

School of Chemistry, University of Sydney, NSW 2006, Australia
t.hudson@chem.usyd.edu.au

Abstract. Packings in 3-dimensional space were constructed of hard spheres of two radii, $r_A > r_B$. Previous studies have shown that a packing density higher than that possible for equal sized spheres ($\delta^3 = \pi/\sqrt{18}$), can be achieved for much of the range $0 < r_A/r_B \leq 0.623\ldots$. This paper completes the range such that there is no $r_A/r_B \leq 0.623\ldots$ for which the packing density cannot exceed that of optimally packed equal spheres.

MSC 2000: 52C07, 52C17
Keywords: packing density, unequal spheres, crystal structure, sphere packing

1. Introduction and definitions

Packing has long captured the interests of geometers, Kepler's conjecture remained open for one of the longest periods in mathematics. The extension of the equal sphere packing problem into n dimensions is also of interest [8]. However important problems still exist for spheres in three dimensional space. One such problem is to determine the densest packings for binary sphere systems [29]. These dense packings are of interest, particularly to materials scientists, as they form spontaneously in systems comprised of hard spherical objects, under high concentration or high pressure conditions [10], [27], [22], [1]. This paper shows, for a broad range of radius ratios, that denser binary sphere packings exist than the face-centred cubic lattice. As such, mixtures of these sizes will preferentially adopt compound sphere packings rather than segregated structures.

Let $B^d \subset E^d$ denote the unit ball in Euclidean d-space, E^d, and let $B_i^d = \vec{c}_i + r_i B^d$ where $i \in 1, 2, \ldots$ If every r_i is equal to either $r_A = \gamma$ with $\gamma \in (0, 1]$ or

$r_B = 1$, (thus $r_A/r_B = \gamma$), and if

$$P^d(\gamma) = \{B_i^d \subset E^d \mid i = 1, 2, \dots \text{with } (\text{int}(B_i^d) \cap \text{int}(B_j^d)) = \emptyset \; for \; i \neq j\}, \quad (1)$$

then $P^d(\gamma)$ is a binary packing of balls.

Let $\delta(P^d(\gamma))$ be the density of the infinite packing $P^d(\gamma)$. If $C^d(x_j) \subset E^d$ denotes a rectangular prism with dimensions $\{x_j\}$ where $j = 1, 2 \dots d$ then its volume is $V(C^d(x_j)) = \prod_{j=1 \dots d} x_j$, and the density is defined as

$$\delta\big(P^d(\gamma)\big) = \lim_{x_j \to \infty | \forall j} \frac{\sum_{B_i^d \subset C^d(x_j^d)} V\left(B_i^d\right) \mid B_i^d \in P^d(\gamma)}{V(C^d(x_j))}. \quad (2)$$

The set of all binary packings of a given radius ratio is denoted by $\mathcal{P}^d(\gamma)$. Then the maximal obtainable density of packings at that radius ratio is

$$\delta^d(\gamma) = \sup\{\delta(P^d(\gamma)) \mid P^d(\gamma) \in \mathcal{P}^d(\gamma)\}. \quad (3)$$

$\delta^d(1)$ corresponds to the maximal obtainable density of packings where all spheres are congruent, denoted δ^d. At the other extreme, we define $\delta^d(0) = \lim_{\gamma \to 0} \delta^d(\gamma)$, then

$$0 < \delta^d(\gamma) < 1 \text{ for } 0 \leq \gamma \leq 1. \quad (4)$$

It is then meaningful to compare $\delta(P^d(\gamma))$ with δ^d, and the optimal lattice packing density δ_L^d. We now define

$$\hat{\gamma}^d = \sup\{\gamma \mid \delta^d(P^d(\gamma)) > \delta^d\}, \text{ and} \quad (5)$$

$$\hat{\gamma}_L^d = \sup\{\gamma \mid \delta^d(P^d(\gamma)) > \delta_L^d\}. \quad (6)$$

2. Known results

For single-sized balls with $d = 2, 3$ the lattice has been shown to be optimal, i.e. $\delta^d = \delta_L^d$, so for these dimensions $\hat{\gamma}^d = \hat{\gamma}_L^d$. The value of δ^2 is $\pi/\sqrt{12}$ [28]. The value of δ^3 is $\pi/\sqrt{18}$ (the result of the proof of Kepler's conjecture [16], [17], [21], [18], [19], [15], [20]). The value of δ_L^d is also known for $4 \leq d \leq 8$ ([8] p. 12, [23], [24], [2], [7]) and $d = 24$ [6], [7].

In binary systems the inequality

$$\delta^d(0) \geq \delta^d + (1 - \delta^d)\delta^d, \quad (7)$$

is obvious since the right hand side can be approximated if we fill the gaps of a densest packing by very small balls, so that the density of the small balls relative to the vacant space is close to δ^d. For $d = 2$, this is the best that can be achieved, so $\delta^d(0) = \delta^d(2 - \delta^d)$ ([13] p. 71 ff.). This means that $\delta^d(\gamma) > \delta^d \geq \delta_L^d$ for small γ, so $\hat{\gamma}$ and $\hat{\gamma}_L$ are nonzero for all $d > 1$. An upper bound for $\hat{\gamma}^d$ has been found for $d = 2$, $\hat{\gamma}^2 \leq 0.74299\dots$ [5], [3], [11], (as has a supremum for the densities of packings with lower γ [4]), but it is an open question whether $\hat{\gamma}^d < 1$ for $d \geq 3$. Lower bounds for $\hat{\gamma}^d$ have been established for those dimensions where δ^d is known, $\hat{\gamma}^2 \geq 0.645\ldots$ ([26],[12] p. 184), and $\hat{\gamma}^3 \geq 0.623\ldots$ [29].

Furthermore it has been shown that $\delta(P^2(\gamma)) > \delta^2$ for all $0 < \gamma < 0.645\ldots$ [14]. In other words there is always a more efficient packing structure for two circles than the classical lattice, up to the established lower bound. The goal of this paper is to prove the analogue in three dimensions.

In the range, $0 < \gamma < 0.623\ldots$, below the current lower bound on $\hat{\gamma}^3$, it is known that

$$\delta(P^3(\gamma)) > \delta^3_L \text{ for } \gamma < 0.444\ldots \text{ and } 0.482\ldots < \gamma < 0.623\ldots. \tag{8}$$

However the gap left wherein remains incomplete [29], [9].

3. Theorems

Theorem 1.

$$\delta(P^3(\gamma)) > \delta^3_L \textit{ for all } \gamma \leq 0.623\ldots$$

Theorem 1 will be here broken into five parts, each occupied by a different packing. Part one, proven by Vassallo and Wills [29] covers the range $\gamma < 0.444\ldots$. Part two is proven in Lemma 1 covering the range $0.444\ldots \leq \gamma < 0.474\ldots$. Then, part three in Lemma 2, covering $0.474\ldots \leq \gamma \leq 0.482\ldots$. Part four, proven by de Lucia [9] covers $0.482\ldots < \gamma \leq 0.577\ldots$ and part five, also proven by Vassallo and Wills [29] covers $0.577\ldots < \gamma < 0.623\ldots$.

The structures we will use to prove Lemmas 1 and 2 are based on hard sphere simulation results previously published [25]. The simulations tested only particular values of γ. We show here that continuous distortions of these structures exceed δ^3 over all γ in the vicinity of these simulation results.

Let L_k denote a large sphere $\vec{l}_k + B^3_k$ of radius 1, and let S_k denote a small sphere $\vec{s}_k + \gamma B^3_k$ of radius γ. The condition for spheres in a packing to be disjoint (equation (1)) can be restated as

$$\begin{aligned} \forall_{i,j} \|\vec{s}_i - \vec{l}_j\| &\leq 1 + \gamma, \\ \forall_{i,j\neq i} \|\vec{s}_i - \vec{s}_j\| &\leq 2\gamma, \text{ and} \\ \forall_{i,j\neq i} \|\vec{l}_i - \vec{l}_j\| &\leq 2. \end{aligned} \tag{9}$$

Lemma 1. *Structure* 1 *has* $\delta(P^3_1(\gamma)) > \delta^3$ *for all* $0.444\ldots \leq \gamma < 0.474\ldots$.

$P^3_1(\gamma)$ consists of a periodic packing of unit cells. The unit cell is a rectangular prism with periodicity of $[4x_3, 2y_1, 4z_3]$. Each unit cell contains four large and four small spheres, arranged within the cell as shown in Figure 1.

For each $k \in 1, 2, 3, 4$, let the location of the centres of the spheres L_k be $\vec{l}_1 = (0, 0, 0)$, $\vec{l}_2 = (2x_3 + 2x_1, y_1, 2z_1)$, $\vec{l}_3 = (2x_1, y_1, 2z_3)$, $\vec{l}_4 = (2x_3, 0, 2z_3)$.

Similarly for spheres S_k let $\vec{s}_1 = (x_3 + x_1 - x_2, 0, z_3 + z_1 - z_2)$, $\vec{s}_2 = (3x_3 + x_1 + x_2, 0, z_3 + z_1 + z_2)$, $\vec{s}_3 = (x_3 + x_1 - x_2, y_1, 3z_3 + z_1 + z_2)$, $\vec{s}_4 = (3x_3 + x_1 -$

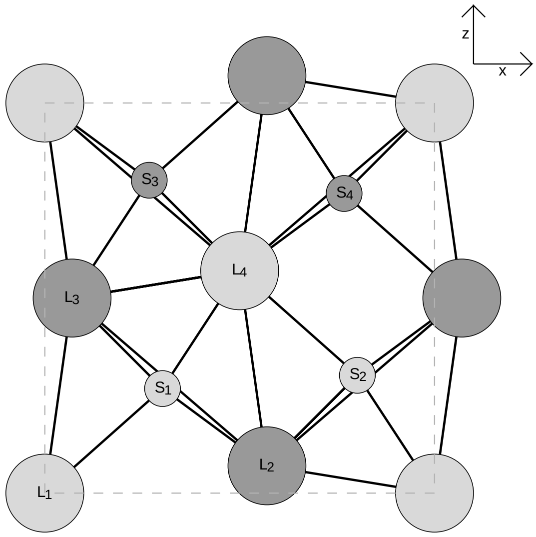

Figure 1. A graphical depiction of structure 1: L_i represent large spheres of radius 1, and S_i represent small spheres of radius γ. Light grey denotes spheres centred in the x-z plane. Dark grey denotes spheres translated by y_1 in the y direction. The dashed grey box denotes the unit cell boundary. Black lines represent contact between spheres. This structure has a density greater than that of the face centred cubic lattice over the radius ratio range $0.414\ldots \leq \gamma \leq 0.474\ldots$.

$x_2, y_1, 3z_3 + z_1 - z_2$), where $x_1, x_2, x_3, y_1, z_1, z_2, z_3$ are positive scalar quantities and $x_1, x_2 < x_3$ and $z_1, z_2 < z_3$.

To ensure a high density, the bonds denoted in Figure 1 (and their periodic images) were minimised to ensure the spheres were in contact, which required that their corresponding equations from equation (9) were equalities rather than inequalities. This yielded a set of seven equations with eight variables, with solutions for each parameter in terms of γ (equation set (10)).

Where $a = (1+\gamma)^2$,

$$\begin{aligned}
x_1 &= \frac{(a-2)(a+4)}{2\sqrt{a}\sqrt{(a+4)(a^2-3a+4)}} \\
x_2 &= \frac{(3a-4)(a^2-3a+4) - \sqrt{(4-3a)^2}}{2(a-2)\sqrt{a}\sqrt{a+4}\sqrt{a^2-3a+4}} \\
x_3 &= \frac{a^{3/2}}{\sqrt{a^3+a^2-8a+16}} \\
y_1 &= \sqrt{3-\frac{4}{a}} \\
z_1 &= \frac{\sqrt{9a^2-24a+16}}{\sqrt{4a^3+4a^2-32a+64}}
\end{aligned}$$

$$z_2 = \frac{(a-2)(\sqrt{(4-3a)^2}+a)}{4\sqrt{(a+4)(a^2-3a+4)}}$$
$$z_3 = \frac{\sqrt{a+4}}{\sqrt{4a^2-12a+16}}. \quad (10)$$

The range of validity of this structure is determined by two factors. The first is that for valid γ, equation set (10) must have real solutions. Secondly, the inequalities in equation (9) must also be satisfied in regard to pairs of spheres not labelled as always in contact. In this case the limits of the range occur at $\sqrt{2}-1 \leq \gamma \leq 0.601\ldots$ [1], (approximately $0.414\ldots \leq \gamma \leq 0.601\ldots$). The lower limit corresponds to contact between spheres S_2 and the periodic image of L_1 displaced by one unit cell in both the x and z directions. The upper limit corresponds to contact between any L_i and its periodic image displaced by one unit cell in the y direction.

The packing density is

$$\delta(P_1^3(\gamma)) = \frac{\pi(\gamma^3+1)}{6x_3y_1z_3} \quad (11)$$

which, in the range of validity, exceeds δ^3 for $\gamma \leq 0.474\ldots$ and $\gamma \geq 0.590\ldots$.

So this structure has $\delta(P_1^3(\gamma)) > \delta^3$ for all $0.414\ldots \leq \gamma < 0.474\ldots$. It is also higher in a later range ($0.590\ldots < \gamma < 0.601\ldots$) however it is unnecessary to consider this in the light of previous work [29]. □

Lemma 2. *Structure* 2 *has* $\delta(P_2^3(\gamma)) > \delta^3$ *for all* $0.471\ldots \leq \gamma \leq 0.482\ldots$.

$P_2^3(\gamma)$ consists of a periodic packing of rectangular unit cells. The cells have a periodicity of $[2x_4+4x_3, y_1, 2z_3]$. Each unit cell contains four large and four small spheres arranged as follows.

For each $k \in 1,2,3,4$, let the location of the centres of the spheres L_k be $\vec{l_1} = (0,0,0)$, $\vec{l_2} = (x_4, y_1, z_3)$, $\vec{l_3} = (x_4+2x_3, 0, z_3+z_1)$, $\vec{l_4} = (2x_4+2x_3, y_1, z_1)$.

Similarly for spheres S_k let $\vec{s_1} = (x_3+x_4-x_1, 0, 0)$, $\vec{s_2} = (x_3+x_4+x_1, y_1, z_1)$, $\vec{s_3} = (3x_3+2x_4-x_1, 0, z_3+z_1)$, $\vec{s_4} = (3x_3+2x_4+x_1, y_1, z_3)$, where $x_1, x_3, x_4, y_1, z_1, z_3$ are positive scalar quantities and $x_1 < x_3, x_4$ and $z_1 < z_3$.

The same methodology as used in Lemma 1, applied to the bonds denoted in Figure 2 gives the following optimized values of the parameters in terms of γ(again the change of variable $a = (1+\gamma)^2$ is used).

[1]The exact value of the upper limit is the positive real root of $\gamma^4+4\gamma^3+5\gamma^2+2\gamma-4=0$.

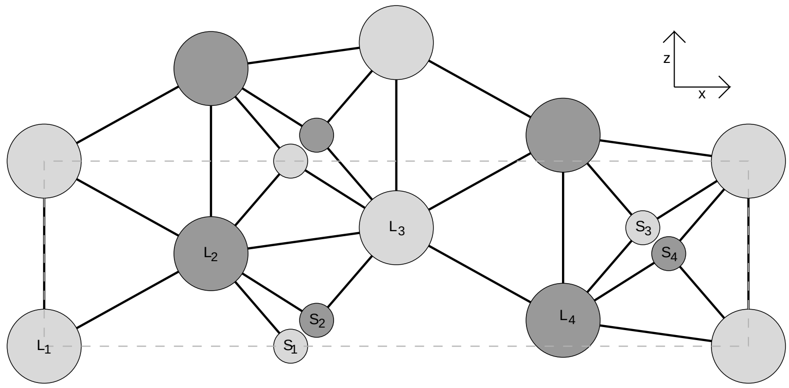

Figure 2. A graphical depiction of structure two: L_i represent large spheres of radius 1, and S_i represent small spheres of radius γ. Light grey denotes spheres centred in the x-z plane. Dark grey denotes spheres translated by y_1 in the y direction. The dashed grey box denotes the unit cell boundary. Black lines represent contact between spheres. This structure has a density greater than that of the face centred cubic lattice over the radius ratio range $0.414\ldots \leq \gamma \leq 0.528\ldots$.

$$\begin{aligned}
x_1 &= \left(a - 1 - \sqrt{(a-2)(3a-4)}\right)\sqrt{\frac{1}{-6+4a-2\sqrt{3a^2-10a+8}}} \\
x_3 &= \sqrt{\frac{1}{4a-6-2\sqrt{3a^2-10a+8}}} \\
x_4 &= \sqrt{2} \\
y_1 &= 1 \\
z_1 &= \frac{1-\sqrt{3a^2-10a+8}}{a-1} \\
z_3 &= 1
\end{aligned} \tag{12}$$

with a range of validity of $\sqrt{2} - 1 \leq \gamma \leq \sqrt{7/3} - 1$, (approximately $0.414\ldots \leq \gamma \leq 0.528\ldots$). The lower bound corresponds to contact between spheres L_4 and the periodic image of L_1 displaced by one unit cell in both the x and z directions. The upper bound corresponds to simultaneous contact between S_1 and L_3, S_4 and the periodic image of L_4 displaced once in the z direction, S_3 and the periodic image of L_1 displaced once in the x direction as well as L_2 and the periodic image of S_2 displaced once in the z direction.

The packing density is

$$\delta(P_2^3(\gamma)) = \frac{\sqrt{2}(1+\gamma^3)\pi}{3\left(1+\left(2\gamma^2+4\gamma-1-\sqrt{3\gamma^4+12\gamma^3+8\gamma^2-8\gamma+1}\right)^{-1/2}\right)} \tag{13}$$

which is real-valued for $\gamma \geq \sqrt{2}-1$, and exceeds δ^3 over the entire range for which it is a valid structure: $\sqrt{2}-1 \leq \gamma \leq \sqrt{7/3}-1$, covering the required range of this lemma. One may note that this also covers the range of Lemma 1, however the packing density of structure 2 is inferior to that of structure 1 for $\gamma < 0.471\ldots$. $\square$

Thus it has been proven that binary sphere packings exist over the entire range $0 \leq \gamma < 0.623\ldots$ for which $\delta(P^3(\gamma)) > \delta^3$.

References

[1] Barlett, P.; Ottewill, R. H.; Pusey, P. N.: *Superlattice formation in binary mixtures of hard-sphere colloids.* Phys. Rev. Lett. **68**(25) (1992), 3801–3804.

[2] Blichfeldt, H. F.: *The minimum values of positive quadratic forms in six, seven and eight variables.* Math. Z. **39** (1934), 1–15. Zbl 0009.24403

[3] Blind, G.: *Über Unterdeckungen der Ebene durch Kreise.* J. Reine Angew. Math. **236** (1969), 145–173. Zbl 0174.25502

[4] Blind, G.: *Unterdeckung der Ebene durch inkongruente Kreise.* Arch. Math. **26**(4) (1975), 441–448. Zbl 0305.52011

[5] Böröczky, K.: unpublished, but see MR0377702 (51#13871).

[6] Cohn, H.; Kumar, A.: *The densest lattice in twenty-four dimensions.* Electron. Res. Announc. Am. Math. Soc. **10** (2004), 58–67. Zbl 1062.11044

[7] Cohn, H.; Kumar, A.: *Optimality and uniqueness of the Leech lattice among lattices.* Ann. Math. **170**(3) (2009), 1003–1050.

[8] Conway, J. H.; Sloane, N. J. A.: *Sphere packings lattices and groups.* Grundlehren Math. Wiss. **290** (1999), third edition, Springer-Verlag. Zbl 0915.52003

[9] De Lucia, L.: *On the radial ratio in dense mixed sphere packings.* Beitr. Algebra Geom. **36** (1995), 145–148. Zbl 0824.52021

[10] Eldridge, M. D.; Madden, P. A.; Frenkel, D.: *Entropy-driven formation of a superlattice in a hard-sphere binary mixture.* Nature **365**(2) (1993), 35–37.

[11] Fejes Tóth, G.: *Covering the plane by convex discs.* Acta Math. Acad. Sci. Hung. **23** (1972), 263–270. Zbl 0252.52006

[12] Fejes Tóth, L.: *Regular figures.* Pergamon Press, New York 1964. Zbl 0134.15705

[13] Fejes Tóth, L.: *Lagerungen in der Ebene, auf der Kugel und im Raum.* Springer, Berlin 1972. Zbl 0229.52009

[14] Fejes Tóth, L.: *Some density bounds for packing and covering with incongruent circles.* Stud. Sci. Math. Hung. **15** (1980), 63–70. Zbl 0514.52009

[15] Ferguson, S. P.: *Sphere packings, V. Pentahedral prisms.* Discrete Comput. Geom. **36**(1) (2006), 167–204. Zbl pre05614955

[16] Hales, T. C.: *A proof of the Kepler conjecture.* Ann. Math.(2) **162**(3) (2005), 1065–1185. Zbl 1096.52010

[17] Hales, T. C.: *Historical overview of the Kepler conjecture.* Discrete Comput. Geom. **36**(1) (2006), 5–20. Zbl pre05614951

[18] Hales, T. C.: *Sphere packings, III. Extremal cases.* Discrete Comput. Geom. **36**(1) (2006), 71–110. Zbl pre05614953

[19] Hales, T. C.: *Sphere packings, IV. Detailed bounds.* Discrete Comput. Geom. **36**(1): (2006), 11–166. Zbl pre05614954

[20] Hales, T. C.: *Sphere packings, VI. Tame graphs and linear programs.* Discrete Comput. Geom. **36**(1) (2006), 205–265. Zbl pre05614956

[21] Hales, T. C.; Ferguson, S. P.: *A formulation of the Kepler conjecture.* Discrete Comput. Geom. **36**(1) (2006), 21–69. Zbl pre05614952

[22] Kiely, C. J.; Fink, J.; Brust, M.; Bethell, D.; Schiffrint, D. J.: *Spontaneous ordering of bimodal ensembles of nanoscopic gold clusters.* Nature **396** (1998), 444–446.

[23] Korkine, A.; Zolotareff, G.: *Sur les formes quadratique positive quaternaires.* Clebsch Ann. **V** (1872), 581–583. JFM 04.0081.03

[24] Korkine, A.; Zolotareff, G.: *Sur les formes quadratique positives.* Clebsch Ann. **XI** (1877), 242–292. JFM 09.0139.01

[25] Kummerfeld, J. K.; Hudson, T. S.; Harrowell, P.: *The densest packing of AB binary hard-sphere homogeneous compounds across all size ratios.* J. Phys. Chem. B **112** (2008), 10773–10776.

[26] Molnár, J.: *Unterdeckung und Überdeckung der Ebene durch Kreise.* Ann. Univ. Sci. Budap. Rolando Eötvös, Sect. Math. **2** (1959), 33–40. Zbl 0098.35604

[27] Murray, M. J.; Sanders, J. V.: *Close-packed structures of spheres of two different sizes II. the packing densities of likely arrangements.* Philos. Mag. A **42**(6) (1980), 721–740.

[28] Thue, A.: *Omnogle geometrisk taltheoretiske Theoremer.* Naturforskermde (1892), 352–353.

[29] Vassallo, S.; Wills, J.: *On mixed sphere packings.* Beitr. Algebra Geom. **35** (1994), 67–71. Zbl 0806.52019

Received October 31, 2008