Densest binary sphere packings

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Abstract

The densest binary sphere packings in the $\alpha$-$x$ plane of small to large sphere radius ratio $\alpha$ and small sphere relative concentration $x$ have historically been very difficult to determine. Previous research had led to the prediction that these packings were composed of a few known “alloy” phases including, for example, the AlB$_2$ (hexagonal $\omega$), HgBr$_2$, and AuTe$_2$ structures, and to XY$_n$ structures composed of close-packed large spheres with small spheres (in a number ratio of $n$ to 1) in the interstices, e.g., the NaCl packing for $n = 1$. However, utilizing an implementation of the Torquato-Jiao sphere-packing algorithm [S. Torquato and Y. Jiao, Phys. Rev. E 82, 061302 (2010)], we have discovered that many more structures appear in the densest packings. For example, while all previously known densest structures were composed of spheres in small to large number ratios of one to one, two to one, and very recently three to one, we have identified densest structures with number ratios of seven to three and five to two. In a recent work [A. B. Hopkins, Y. Jiao, F. H. Stillinger, and S. Torquato, Phys. Rev. Lett. 107, 125501 (2011)], we summarized these findings. In this work, we present the structures of the densest-known packings and provide details about their characteristics. Our findings demonstrate that a broad array of different densest mechanically stable structures consisting of only two types of components can form without any consideration of attractive or anisotropic interactions. In addition, the novel structures that we have identified may correspond to currently unidentified stable phases of certain binary atomic and molecular systems, particularly at high temperatures and pressures.

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I. INTRODUCTION

A packing is defined as a set of nonoverlapping objects arranged in a space of given dimension \( d \), and its packing fraction \( \phi \) is the fraction of space that the objects cover. Packings of spheres in \( d \)-dimensional Euclidean space \( \mathbb{R}^d \) are frequently used as starting points in modeling atomic, molecular, and granular materials consisting of particles exhibiting strong repulsive pair interactions at small particle separations. In particular, the densest sphere packings in \( \mathbb{R}^d \), or packings with maximal packing fraction \( \phi_{\text{max}} \), often correspond to ground states of systems of particles with pairwise interactions dominated by steep isotropic pairwise repulsion \cite{1}. For example, see the ground states in Refs. \cite{2,3,4,5,6}.

Packings of identical spheres have been employed in \( \mathbb{R}^3 \) to describe the structures and some fundamental properties of a diverse range of substances from crystals and colloids to liquids, amorphous solids and glasses \cite{8,9,10,11}. Despite their simplicity, complicated structures and interesting properties can arise in packings of identical spheres through simple principles like density maximization in a confined space \cite{12,13}. Packings of identical nonspherical objects in \( \mathbb{R}^3 \) have also been studied, though not to the extent of sphere packings, and have applications, for example, in the self-assembly of colloids and nanoparticles \cite{14,15,16,17,18,19}. In structural biology, molecular dynamics simulations of interactions between large numbers of molecules employ chains of identical nonoverlapping spheres as models for various biological structures such as proteins and lipids \cite{21}, and packing of nonspherical objects of different sizes are used, for example, in tumor growth modeling \cite{22,23}.

Packings of spheres of many different sizes have been employed as structural models for materials such as solid propellants and concrete, among others \cite{24,25}. Dense binary packings of spheres, packings of spheres of only two sizes, have long been employed as models for the structures of a wide range of alloys \cite{3,26,27,28,29,30,31}. In this work, we focus on binary sphere packings. Though they are relatively simple models, much about them is still unknown due in part to the enormous binary sphere-packing parameter space of sphere size ratio and relative concentration. Recently, we presented the most comprehensive determination to date, to the best of our knowledge, of the “phase diagram” in small to large sphere size ratio \( \alpha \) and small sphere relative concentration \( x \) for the densest binary sphere packings in \( \mathbb{R}^3 \) \cite{33}. In the present paper, we extend these results to produce a new phase diagram, and we present a theorem and proof concerning the number of phases present in a densest packing with \( \eta \)...
different types of objects. Additionally, we present detailed structural descriptions of the alloy phases present in the densest packings, identified using the Torquato-Jiao (TJ) determinental sphere-packing algorithm [34], including descriptions of many that were heretofore unknown. Here we use the term “alloy” in a general sense to mean a structure composed of two or more distinguishable components that are not phase-separated.

Structures, or configurations of points, can be classified as either periodic or aperiodic. Roughly defined, a periodic structure (packing) is one consisting of a certain number of points (sphere centers), called the basis, placed in a defined region of space, the unit cell, replicated many times over such that the cells cover all space without any overlap between cells (or spheres). A fundamental cell is one with minimal basis, i.e., such that a smaller fundamental cell and basis with the same periodic structure does not exist. An aperiodic structure is one with an infinite (or in practice, very large finite) minimal basis. By definition, it is clear that a binary sphere packing must have at least two spheres in its minimal basis. Figure 1 is an illustration that compares subsections of periodic and aperiodic packings of monodisperse disks.

The packing fraction \( \phi_{\text{max}}(\alpha, x) \) of the densest binary packings of spheres in \( \mathbb{R}^3 \) is a function only of small to large sphere radius ratio \( \alpha = R_S/R_L \), with \( R_S \) and \( R_L \) the respective radii of the small and large spheres, and small sphere relative concentration \( x \). Specifically, one has,

\[
x \equiv \frac{N_S}{N_S + N_L},
\]

with \( N_S \) and \( N_L \) the respective numbers of small and large spheres in the packing, and when \( N_S + N_L \to \infty \) in the infinite volume limit, \( x \) remains constant. It is implicit in the definition of \( \phi_{\text{max}}(\alpha, x) \) that radii are additive, i.e., two spheres of different radii can be no closer than distance \( R_S + R_L \) from one another. In this work, we focus on the additive case, though we note that the TJ algorithm can be trivially modified to study sphere-packings with non-additive diameters. Past studies of certain sphere packings with non-additive diameters can be found, for example, in Ref. [35].

The densest packings in \( \mathbb{R}^3 \) are composed of a countable number of distinct phase-separated alloy and monodisperse phases. Previously, the only alloys thought to be present in the densest packings for \( \alpha > \sqrt{2} - 1 = 0.414213 \ldots \) corresponded to structures such as the A\(_3\)B, AlB\(_2\) (hexagonal \( \omega \)), HgBr\(_2\), and AuTe\(_2\) structures [27, 36, 38], and to a structure
composed of equal numbers of small and large spheres [39]. For $\alpha \leq \sqrt{2} - 1$, the alloys thought to be present were $XY_n$ structures of close-packed large spheres with small spheres (in a ratio of $n$ to 1) in the interstices, e.g., the NaCl packing for $n = 1$. However, in a recent work [33], we showed that in addition to these alloys, many more are present in the putative densest packings, including several with heretofore unknown structures.

The densest binary packings of spheres can be directly relevant to atomic and molecular phases in binary solids and compounds. For example, structures such as that exhibited by AlB$_2$ have been predicted and observed to be present in high temperature and pressure

![FIG. 1: Illustrations of subsections of packings of disks that are a) periodic and b) aperiodic.](image)
phases of various binary intermetallic and rare-gas compounds [40][41]. Furthermore, phase separation of alloys like that present in the densest binary packings has been observed in certain binary atomic and molecular solids at high temperatures and pressures, conditions where relaxation time scales are fast and diffusion rates high [42]. These observations indicate that the hard-sphere additive-radii interactions that lead to the densest binary sphere packings may be sufficient to determine the stable phases of many binary atomic and molecular solids and compounds at high temperatures and pressures. In addition, we believe that there are binary atomic and molecular systems, particularly at high temperatures and pressures, that will exhibit stable phases with structures corresponding to the heretofore unknown alloys described in Sec. V.

In the past, finding the densest packings has been difficult in part due to the complexity of proving that a packing of spheres in $\mathbb{R}^d$ is the densest possible, evident in that Kepler’s Conjecture concerning the densest packings of monodisperse spheres in $\mathbb{R}^3$ was only recently proved by Hales [43]. In the $\alpha$-$x$ plane, the monodisperse case corresponds to the Kepler limit $\alpha = 1$; in this limit, the packing fraction of the densest packings is $\phi = \pi/\sqrt{18} = 0.740480\ldots$. This fraction is achieved by any of the infinite number of Barlow packings [44], which include the well-known fcc and hcp sphere packings. Some efforts have been made to identify the densest alloy packings away from the limit $\alpha = 1$ by using simple crystallographic techniques [27, 45]; however, these have been limited to only a small subset of possible periodic alloy packings.

Methods such as Monte Carlo [39][46][47] and genetic algorithms [37] have also been employed, with limited success, to attempt to find densest binary sphere packings over certain ranges of $\alpha$ and $x$. In part due to the enormous number of different initial sphere spatial configurations required by these methods to identify densest packings of a large number of spheres, high resolution searches in $\alpha$ and $x$ would previously have required an enormous amount of computational time. As a result, the densest alloys found by past efforts were limited to minimal bases with relatively smaller numbers of spheres, and, aside from the $XY_n$ packings, relative compositions of $x = 1/2$, $x = 2/3$, and very recently, $x = 3/4$ [36]. In contrast, employing an implementation of the TJ sphere-packing algorithm [34], we have found several new alloys for $\alpha > \sqrt{2} - 1$ including three with 12, 10, and 7 spheres in their minimal bases, in respective small to large number ratios of one to one, seven to three, and five to two.
Using the TJ algorithm, an overview of which is given in Sec. III, we have systematically surveyed the parameter space \((\alpha, x) \in [0, 1] \times [0, 1]\), omitting the rectangular area \(\alpha < 0.2\) and \(x > 11/12\) for reasons mentioned below, to find the putative densest binary packings at high resolution in \(\alpha\) and \(x\) for bases of up to 12 spheres. From this survey, we are able to construct the most comprehensive determination to date of the phase diagram of the densest binary packings in \(\mathbb{R}^3\) in the \(\alpha\)-\(x\) plane, and the best known lower bound on the function \(\phi_{\text{max}}(\alpha, x)\) for the values of \(\alpha\) that we survey. Though the representation we construct is technically a lower bound on \(\phi_{\text{max}}(\alpha, x)\) as it excludes densest aperiodic packings and periodic packings with bases greater than 12, we contend (for reasons described in Sec. III) that for the vast majority of \((\alpha, x)\), it is a precise representation of \(\phi_{\text{max}}(\alpha, x)\).

We present different representations of the most comprehensive determination to date of the phase diagram in Figs. 2, 3, 5, 7, and 14. Similar versions of Figs. 2 and 3 were presented in Ref. [33]. In Fig. 5, we describe heretofore unknown alloys by the number of small and large spheres in their minimal bases, e.g., (6-6) for the alloy with six small and six large spheres. In both figures, phase boundaries are drawn between packings with distinct alloys,
where each distinct alloy exhibits a unique lattice system characterization of its fundamental cell and composition of spheres in its minimal basis. In the figures, points (lines) where the composition of phase-separated phases changes from alloy plus monodisperse packing of small spheres to the same alloy plus a monodisperse packing of large spheres are not drawn. In Fig. 5, where only one alloy is listed, it is assumed that the densest packing consists of a monodisperse phase and an alloy phase, except at points such that \( x = S_i/(S_i + L_i) \), with \( S_i \) and \( L_i \) the respective numbers of small and large spheres in the minimal basis of the alloy phase listed, where only the alloy phase is present.

FIG. 3: (Color online) The most comprehensive determination to date of the phase diagram and maximal packing fraction surface \( \phi_{\text{max}}(\alpha, x) \) of the densest binary sphere packings in \( \mathbb{R}^3 \). Note that we have excluded the rectangular region \( \alpha < 0.20, \ x > 11/12 \). Different shading indicates a different phase composition, as specified in Fig. 5.

Each distinct alloy appears in the densest packings over a range of \( \alpha \). However, most alloys exhibit varying contact networks over this range, where a contact network describes the numbers of small and large sphere contacts for each sphere in the minimal basis. Each distinct alloy could thus be subdivided into “suballoys” based on contact networks, as was done for the periodic disk alloys in Ref. [38]. Though we do not make these subdivisions in this work due to the very large number of suballoys that would be identified, we note that there are practical reasons for the subdivision. In particular, subdivision by contact network would allow for characterization of all of the line segments in the \( \alpha-x \) plane along...
which the slope of the surface changes discontinuously. These discontinuities can be clearly seen in Fig. 4 plots of the best-known lower bounds on $\phi_{\max}(\alpha, 1/2)$ and $\phi_{\max}(\alpha, 2/3)$ for $0 \leq \alpha \leq 0.7$. In Fig. 4 $M_S$ and $M_L$ refer to monodisperse, Barlow-packed phases of small and large spheres, respectively.

FIG. 4: (Color online) Plots of the best-known lower bounds on $\phi_{\max}(\alpha, x)$ for $0 \leq \alpha \leq 0.7$ and (a) $x = 1/2$, (b) $x = 2/3$, considering minimal bases up to 12 spheres. Coloration (shading) in these plots indicates the phases present in the densest packings, as described in the legend.

One example of a discontinuity in slope occurring along a line segment inside a phase region is for the highest point in Figs. 2 and 3 at $\phi_{\max}(0.224744\ldots, 10/11) = 0.824539\ldots$. If this phase region was subdivided according to the contact networks of the alloys that compose the phase, this point would occur along a phase boundary. Another example is found in the alloy with triclinic lattice system characterization with six small spheres and one large sphere in its minimal basis, present in the densest packings over the range $0.292 \leq \alpha \leq 0.344$. In Figs. 2, 3 and 5 to serve as an example, the phase region including
this alloy has been subdivided according to the number of large-large sphere contacts in the alloy. There are eight, six, and four large-large sphere contacts, respectively, in the (6-1)$_8$, (6-1)$_6$, and (6-1)$_4$ “suballoys”, and close inspection of the bottom plot in Fig. 4 reveals discontinuous changes in slope in $\alpha$ at each of the boundaries between them.

In general, the surface presented in Figs. 2 and 3 is continuous and piecewise differentiable, though as $\alpha \to 0$ and $x \to 1$, the density of curves along which the surface is not differentiable approaches infinity due to the number of $XY_n$ and similar packings. For this reason, we exclude the region $\alpha < 0.2$, $x > 11/12$ from our study, truncating $\alpha$ at 0.2 because it is close to the maximum value $\alpha = 0.216633\ldots$ at which 11 small spheres fit in the interstices of a close-packed Barlow packing of large spheres. For $\alpha > 0.660\ldots$, we have been unable to find any periodic packing with basis of 12 or fewer spheres that exceeds the packing fraction $\pi/\sqrt{18}$ of two phase-separated monodisperse Barlow-packed phases.

Away from the point $(\alpha, x) = (0, 1)$, we represent the surface at given $\alpha$ piecewise-analytically in $x$. This is possible because densest packings can be constructed from a finite number of phase-separated alloy and Barlow-packed monodisperse phases, where phase-separated packings are the densest since the interfacial volume of the boundaries between phases is negligible in the infinite volume limit. Further, we prove in Sec. [IV] that at any point $(\alpha, x)$ with $\alpha > 0$, $x < 1$, there is at least one densest binary packing that consists of no more than two phases. However, this does not preclude the possibility of a densest packing consisting of more than two distinct phases, nor the possibility of “mixing” of phases in certain specific cases where there is no boundary cost.
In Sec. II, differences between periodic, aperiodic, disordered, and quasicrystalline packings are described. We discuss which types of packings are found to be the densest in \( \mathbb{R}^2 \), and which we have been able to find (and predict to find) in \( \mathbb{R}^3 \). In Sec. III, an overview of the TJ algorithm is provided that includes reasons why the algorithm is particularly successful in identifying dense alloys. In Sec. IV, we describe precisely the method used to construct the maximal-density surface \( \phi_{\text{max}} \) and present a proof of why for \( \eta \) different sizes of spheres in any dimension \( d \), there is always a densest packing consisting of only \( \eta \) phase-separated phases. In Sec. V, the structural details of the putative densest binary sphere packings in \( \mathbb{R}^3 \) for minimal bases of 12 or fewer spheres are presented and their properties discussed. In Sec. VI, we conclude with the goals of related future research and the implications and applications of our findings.

II. PERIODIC PACKINGS, APERIODIC PACKINGS, AND JAMMING

The space of binary sphere packings in \( \mathbb{R}^d \) can be formed from a configuration of points where there are \( N_S \) points designated type \( S \) and \( N_L \) points designated type \( L \). Each pair of points of type \( S \) must be separated by at least a distance \( 2R_S \), each pair of points of type \( L \) by at least a distance \( 2R_L \), and each pair including one point of each type by at least distance \( R_S + R_L \). With the points representing sphere centers, this construct describes the space of all binary packings of small (S) and large (L) spheres in \( \mathbb{R}^d \) with radius ratio \( \alpha = R_S/R_L \) and small sphere relative concentration \( x = N_S/(N_S + N_L) \).

Configurations of points can be categorized by their spatial distributions. In this way, all packings can be described as lattice, periodic, or aperiodic. A lattice \( \Lambda \) in \( \mathbb{R}^d \) is a subgroup consisting of the integer linear combinations of a given set of \( d \) lattice vectors that span \( \mathbb{R}^d \). This is referred to as a Bravais lattice in the physical sciences and engineering. A lattice packing of identical nonoverlapping objects is one in which the objects have centers located at the points of \( \Lambda \). In a lattice packing, the space \( \mathbb{R}^d \) can be geometrically divided into identical regions called fundamental cells, each of which contains the center of only one object. For a lattice packing of spheres, which are necessarily identical, the packing fraction \( \phi \) in \( \mathbb{R}^d \) is given by,

\[
\phi = v_1(R)/V_F,
\]  

(2)
with $R$ the radius of the spheres, $V_F$ the volume of the fundamental cell, and

$$v_1(R) = \pi^{d/2} R^d / \Gamma(1 + d/2)$$  \hspace{1cm} (3)

the volume of a single sphere, where $\Gamma(x)$ is the Euler gamma function.

An extension of the notion of a lattice packing is a periodic packing. A periodic packing is obtained by placing a fixed configuration of the centers of $N \geq 1$ objects, called the *basis*, in one cell of a lattice $\Lambda$, and then replicating this fixed configuration, without overlap, in all other cells. The cell in this case is termed a *unit cell*, and is also a fundamental cell with corresponding *minimal basis* if and only if no smaller unit cell (with fewer than $N$ object centers) can describe the same packing. In either case, the packing fraction for a packing of spheres, not necessarily identical in size, is given by,

$$\phi = \sum_{i=1}^N v_1(R_i) / V_U,$$  \hspace{1cm} (4)

with $R_i$ the radius of each sphere in the basis and $V_U$ the volume of the cell. It is critical to note that no binary packing with $0 < x < 1$ can be a lattice packing, since the basis of a binary packing by definition must consist of at least two objects.

An aperiodic packing is one that exhibits no long-range translational order; *i.e.*, its minimal basis is equal to the number of particles in the packing. Practically speaking though, a packing with a very large number of objects might be called aperiodic if it is comprised of only a few translations of the minimal basis. Both periodic and aperiodic structures are found widely in nature; examples of the former include crystalline solids like many metals and salts, and examples of the latter include liquids, glasses, gels, gases, plasmas and quasicrystals [48].

A quasicrystal is an aperiodic structure that nonetheless exhibits bond orientational order in symmetries (*e.g.*, five-fold) forbidden to periodic crystals. We refer the reader to Ref. [49] for a more precise definition. We describe a *directionally periodic* structure as an aperiodic structure that exhibits a period along at least one spatial axis but never simultaneously along $d$ lattice vectors, *e.g.*, a random stacking Barlow packing.

The Barlow packings are constructed by stacking layers, each consisting of contacting spheres in $\mathbb{R}^3$ with centers on a plane in a triangular lattice configuration, on top of one
another. There are two ways (layers in positions $B$ and $C$) to stack such a layer on top of another (layer in position $A$) such that all spheres in each layer are in contact with three spheres in the adjacent layer. Any packing that is composed of an infinite number of $A$, $B$, and $C$ layers, with no adjacent layers the same, is a Barlow packing and achieves the maximal packing fraction of identical spheres in $\mathbb{R}^3$. A random stacking of layers according to these rules is a random stacking Barlow packing, which exhibits periodicity parallel to the planes of the layers but not perpendicular to them.

For the purposes of this paper, we describe a *disordered* structure as an aperiodic structure that does not exhibit perfect long-range symmetry, translational, rotational, or reflective, of any kind.

In $\mathbb{R}^2$, periodic, quasicrystalline, and directionally periodic structures can all be found among the putative densest binary disk packings \cite{38, 50–52}. We believe that all of these types of structures may be found among the densest binary sphere packings in $\mathbb{R}^3$ as well, though we have identified only periodic and directionally periodic structures in this work. Due to computational constraints attributable in large part to the scope and resolution of our survey in $(\alpha, x)$, we have limited our survey in this work to investigating the densest periodic packings with bases of 12 spheres or fewer. This limitation substantially increases the difficulty of identifying aperiodic packings, which most often cannot be approximated well by a fundamental cell with a basis of only 12 spheres, though densest directionally periodic packings often can still be identified by extrapolating from periodic packings.

One property of a densest packing is that a subset of its objects is *collectively jammed*, or in the case of a densest periodic packing, that the objects within each unit cell are *strictly jammed* under periodic boundary conditions. None of the nonoverlapping objects in a packing that is *locally jammed* can be continuously displaced (displaced by infinitesimally small movements) without displacing one of its neighbors \cite{53}. In a collectively jammed packing, a subset of the objects (the *backbone*) is locally jammed and no continuous collective motion of any subset of objects can lead to *unjamming*, *i.e.*, a packing that is no longer locally jammed. The objects that can be displaced without displacing their neighbors in a collectively jammed packing are termed *rattlers*. A strictly jammed packing is collectively jammed, and no collective motion of any subset of objects, coupled with a continuous deformation of the boundary that does not increase volume, can result in unjamming. If a subset of the objects in a packing is not collectively or strictly jammed, then by definition
a uniform continuous motion exists that results in free space around the objects, i.e., the packing is not a densest packing because its volume can be reduced.

One reason that the TJ algorithm is particularly effective at finding densest periodic packings is that it guarantees that final packings are strictly jammed. If there is a collective continuous motion of the spheres, coupled with a uniform continuous deformation of the unit cell, that will decrease the volume of the cell, then the exact linear programming method employed by the TJ algorithm will find that motion.

With respect to jamming, a certain group of packings that we call “host-guest” packings deserves further attention. In such a packing, a subset (usually the larger spheres) of the total packing are packed as a jammed periodic packing, and a mutually exclusive subset (usually the smaller spheres) sit in the interstices formed by the jammed spheres but without contacting the jammed spheres. Clearly, the spheres within the interstices can be continually displaced without altering the density of the packing. In this way, a host-guest packing can be periodic or aperiodic. If the rattlers are placed in the same place relative to one another throughout every cell of the packing, then the packing is periodic. If they are placed at random, then the packing is aperiodic. A host-guest packing is similar in nature to an interstitial solid solution (ISS) phase, such as the stable binary colloidal phases described in Ref. [54]. We are not aware of any densest packings where the large spheres are free to move, as rattlers, within interstices created by jammed small spheres.

The XY$_n$ packings where small spheres are not required to contact the jammed large spheres are good examples of host-guest sphere packings, where an XY$_n$ packing consists of a Barlow-packed structure of contacting large spheres with small spheres placed in the interstices. Among the host-guest packings, one can distinguish topologically between packings where the small spheres are small enough to move freely about all of the interstices and packings where they are confined to a given interstice or finite set of interstices. In the former case, the space available to the small spheres is topologically connected, where in the latter case it is not. Though we find densest packings (e.g., XY$_n$ packings) where small spheres are confined to a single interstice, we do not find for $\alpha \geq 0.2$ any where they are free to move about all of the interstices. However, it is the case for small enough $\alpha$ that there are densest host-guest packings where the space available to the small spheres is topologically connected.
III. THE TORQUATO-JIAO SPHERE-PACKING ALGORITHM

There are several factors that have limited past algorithmic techniques in finding densest packings. As previously discussed, one of these is the immensity of the parameter space in \((\alpha, x)\) of densest binary packings. Another is the strong initial condition dependence of many algorithms, which requires that a very large number of simulations beginning with different initial spatial conditions be undertaken to find a densest packing. This required number of simulations can increase exponentially with the number of spheres simulated.

Past algorithmic techniques have also been limited by the vast multitude of local minima in “energy”, defined as the negative of the packing fraction, present in the phase space of a periodic sphere packing with unit cell of indeterminate size and shape with even a small basis. Methods that move only one sphere at a time cannot escape from local minima where a collective motion of spheres is required to decrease energy, and methods that move several spheres at once rely on chance, and hence a very large number of steps, to find the right collective movement. Many molecular dynamics algorithms rely upon principles of equilibrium thermodynamics, which necessitate that large numbers of time-consuming steps (individual sphere movements) be taken at each stage of sphere growth or compression of the unit cell in order to reduce the chance of becoming “stuck” in a local minimum.

In this paper, we are able to overcome these time and computational limitations by using the Torquato-Jiao linear programming algorithm \cite{34}. The TJ sphere packing algorithm does not easily become “stuck” in local minima because it is inherently designed to find the simultaneous collective linear motion of both the spheres and the unit cell geometry that maximizes the density of the packing.

The TJ algorithm approaches the problem of generating dense, periodic packings of nonoverlapping spheres with an arbitrary size distribution as an optimization problem to be solved using linear programming techniques. In particular, the objective function is chosen to be the negative of the packing fraction (as indicated above), which is minimized with respect to particle (sphere center) positions and the shape and size of the unit cell, subject to sphere nonoverlap conditions. The use of a deformable unit cell, defined in terms of \(d, \) \(d\)-dimensional lattice vectors \(\mathbf{M}_A = \{\lambda_1; \ldots; \lambda_d\}\), was first introduced by Torquato and Jiao \cite{16} to obtain dense packings of hard polyhedral particles including Platonic and Archimedean solids.
For nonoverlapping spheres, the optimization problem can be efficiently solved by linearizing the objective function and nonoverlap constraints. This approach has the advantage of being rigorously exact near the jamming limit of the spheres and unit cell [34].

The TJ algorithm begins with an initial packing of \( N \) spheres, and obtains a new, denser packing by solving the following linear programming problem:

\[
\begin{align*}
\text{minimize: } & \text{Tr}(\varepsilon) = \varepsilon_{11} + \cdots + \varepsilon_{dd} \\
\text{subject to: } & M_\Lambda \cdot r_{ij}^\lambda \cdot \varepsilon \cdot M_\Lambda \cdot r_{ij}^\lambda + \Delta r_{ij}^\lambda \cdot G \cdot r_{ij}^\lambda \geq \frac{1}{2}(\overline{D}_{ij}^2 - r_{ij}^\lambda \cdot G \cdot r_{ij}^\lambda) + R, \\
& \text{for all neighbor pairs } (i, j) \text{ of interest, and} \\
& \Delta x_{i,\text{lower}}^\lambda \leq \Delta x_i^\lambda \leq \Delta x_{i,\text{upper}}^\lambda, \ \forall \ i = (1, \ldots, N), \\
& \varepsilon_{kl,\text{lower}} \leq \varepsilon_{kl} \leq \varepsilon_{kl,\text{upper}}, \ \forall \ k, l = (1, \ldots, d). \\
\end{align*}
\]

where \( \overline{D}_{ij} = (D_i + D_j)/2 \) is the average diameter of spheres \( i \) and \( j \) in the initial packing with respect to the lattice vectors \( M_\Lambda \); \( \Delta r_{ij}^\lambda = \Delta x_i^\lambda - \Delta x_j^\lambda \) is the relative change in displacement of spheres \( i \) and \( j \) in coordinates with respect to the \( M_\Lambda \); \( \varepsilon = \{ \varepsilon_{kl} \} \) is the strain tensor associated with the unit cell, with lower and upper bounds \( \{\varepsilon_{kl,\text{lower}}\} \) and \( \{\varepsilon_{kl,\text{upper}}\} \), respectively; \( G = M_\Lambda^T \cdot M_\Lambda \) is the Gram matrix of the lattice and \( R \) is a scalar representing higher order terms, which are given in Appendix A. The neighbor pairs are determined by an influence sphere with radius \( \gamma_{ij} \), i.e., two spheres \( i \) and \( j \) are considered neighbors if their pair distance is smaller than \( \gamma_{ij} \). We note that the choice of the influence sphere radius can significantly affect the density and degree of disorder in the final packing. For densest packings, a large \( \gamma_{ij} \) should be used, as detailed in Ref. [34]. We also note that to study packings of spheres with non-additive diameters, one simply sets \( D_{ij} \) to the desired value when spheres \( i \) and \( j \) are not of the same type.

Our tests of the TJ algorithm, for which the implementation for binary sphere packings is described in Appendix A, indicate that the algorithm is both particularly efficient and particularly robust in finding densest packings across the entire range of \( (\alpha, x) \) for a sufficiently small basis of spheres. For example, we have recovered all of the alloys known to be present in the densest packings, including the \( A_3B \) [36], \( AlB_2 \), \( HgBr_2 \), \( AuTe_2 \), and “Structure 2” [39].
alloys, and XYₙ packings for certain values of n. In addition, we have found many areas in
the α-x plane where the densest packings are denser than previously predicted and include
heretofore unknown alloys. Overall, in the area of the α-x plane searched, we always recover
a packing fraction φ_max(α, x) that is either greater than or equal to that previously known.

IV. IDENTIFYING THE DENSEST BINARY SPHERE PACKINGS

To identify the densest binary packings in \( \mathbb{R}^3 \), we begin with the obvious statement that
at all given (α, x), there is a densest packing that consists of a finite number of phase-
separated alloy and monodisperse phases. In the infinite volume limit in \( \mathbb{R}^d \) for \( \eta \) different
sizes of spheres, the packing fraction of a phase-separated collection of \( \beta \) monodisperse and
distinct alloy phases can be written,

\[
\phi = \frac{(\pi^{d/2} \Gamma(1 + d/2)) \left( \sum_{j=1}^{\eta} X^{(j)}(R^{(j)})^d \right)}{\sum_{i=1}^{\beta} C_i S_i x_i^F_i},
\]

with \( X^{(j)} \) and \( R^{(j)} \) the relative fraction and radii, respectively, of spheres of type (size) \( j \),
\( x_i^j \) the relative fraction of spheres of type \( j \) distributed in phase \( i \) (\( \sum_{j=1}^{\beta} x_i^j = X^{(j)} \)), and
\( C_i \) the volume of a unit cell of phase \( i \) containing, for each sphere type \( j \), \( S_i^j \) spheres. The
index \( j = F_i \) in \( S_i^{F_i} \) and \( x_i^{F_i} \) is the first index \( j \) in phase \( i \) such that \( S_i^j \neq 0 \). For \( \eta \) sphere
sizes, there are \( \eta \) monodisperse phases with relative fraction \( x_i^{F_i} \), \( F_i = 1 \ldots \eta \) respectively
and \( S_i^{j} = 0 \) for all \( j \neq F_i \), representing packings with spheres packed as densely as possible
in \( \mathbb{R}^d \).

To find the densest packing \( \phi_{max}(R^{(1)} \ldots R^{(\eta)}, X^{(1)} \ldots X^{(\eta)}) \) at specified sphere sizes \( R^{(j)} \)
and relative compositions \( X^{(j)} \) from among \( \beta \) known alloy and close-packed monodisperse
phases, Eq. (6) must be maximized. This is accomplished by minimizing the denominator of
Eq. (6) over the relative fractions \( x_i^{F_i} \). As the denominator is linear in the variables \( x_i^{F_i} \), it can be
formulated as the objective function in a linear programming problem. This formulation
allows us to state the following theorem, the proof of which is found in Appendix B. We
note that Theorem 1 applies not only to spheres, but in fact to any packing of \( \eta \) different
types of objects in \( \mathbb{R}^d \) with specified volumes and relative fractions \( X^{(j)} \).

**Theorem 1.** Consider any sphere packing in \( \mathbb{R}^d \) composed of \( \beta \) phase-separated alloy and
monodisperse phases. For η different sizes of spheres, there is always a densest packing consisting of no more than η phase-separated phases.

For binary sphere packings with η = 2 in \( \mathbb{R}^3 \), it is thus clear that there is at least one densest packing at every \( (\alpha, x) \) consisting of no more than two phases. For simplicity in this case, we set \( X^{(1)} = 1 - x \) to be the relative fraction of large spheres and \( X^{(2)} = x \) the relative fraction of small spheres, and rewrite Eq. (6) as,

\[
\phi = \frac{4\pi}{3} \left( (1 - x) R_L^3 + x R_S^3 \right) \frac{x}{x C_B^S + (1 - x) C_B^L + \sum_{i=1}^{\beta} x_i^L \left( \frac{C_i}{L_i} - \frac{S_i}{L_i} C_B^S - C_B^L \right)} ,
\]

(7)

with \( C_B^S \) and \( C_B^L \) the volume per sphere, respectively, in a close-packed Barlow packing of small and large spheres, \( x_i^L \) the relative fraction of large spheres distributed in alloy phase \( i \), and \( C_i \) the volume of a fundamental cell of alloy phase \( i \) containing \( L_i \) large and \( S_i \) small spheres.

Using Eq. (7) and considering a fixed value of \( \alpha \), the densest binary packings in \( \mathbb{R}^3 \) can be found for all values of \( x \) by solving for all globally optimal vertices considering all dense alloy phases at \( \alpha \). Since we limit ourselves in this work to minimal bases of no more than 12 spheres, we must assume that all of these alloy phases can be constructed from repetitions of local structures consisting of 12 spheres or fewer. Though we recognize that this assumption is most likely false for some values of \( \alpha \), especially near the point \( (\alpha, x) = (0, 1) \), we contend that for the majority of the area of the parameter space studied, it is correct. We therefore employ the TJ algorithm to search the space of fundamental cells in \( \mathbb{R}^3 \) containing all combinations of positive integer \( L_i \) and \( S_i \) such that \( L_i + S_i = 2, 3, \ldots, 12 \). We have solved these problems (putatively) to accuracy of about \( 10^{-4} \) in \( \phi \) for \( \alpha \) spaced 0.025 apart, and on a finer grid with \( \alpha \) spaced about 0.0028 apart for certain values of \( S_i \) and \( L_i \) where particularly dense packings were identified.

V. PACKING RESULTS

In the following subsections, the densest binary sphere packings that we have identified are presented, including both those that were previously known and those that, to the best of our knowledge, were not. For those alloys that were not previously known, in Table I in
Appendix C we list packing fractions across the range of $\alpha$ where they appear in the densest packings. In subsection V A, we discuss some of the properties of these packings, including, for example, the lattice symmetry of alloy phases present in the packings and classification of these phases as periodic or aperiodic. The properties that we discuss do not serve as an exhaustive list, nor are the examples we provide the only examples of densest binary packings with these properties. Instead, we discuss packing properties with the intent of providing an overview of the diversity of the different types of densest packings.

The figures presented in this section are illustrations of unit cells of the alloys that appear in the densest packings, where the unit cells are chosen to highlight packing symmetry. Contacts between two large spheres are indicated by dotted lines, as are contacts between two small spheres; however, large-small contacts are not drawn. Unit cell boundaries are also indicated by dotted lines, and unit cell boundary lengths are displayed in units of the diameter of the large spheres. Angles are given in degrees.

A. Packing properties

The densest binary sphere packings that we have identified exhibit a broad array of properties. For example, there are densest packings that consist of only a single phase, and many that consist of multiple phases. In the majority of these phases, all spheres are collectively jammed. In others, each fundamental cell contains rattlers, i.e., there are an infinite number of sphere configurations in each cell that exhibit the same packing fraction. In others still, there are only a finite number of sphere configurations in each cell that exhibit identical packing fraction.

Concerning rattlers in densest packings, it is intuitive that for the majority of the volume of the parameter space of densest packings of $\eta$ different sizes of spheres, packings with rattlers would dominate as $\eta$ increases. This is because for densest packings with substantial size disparity between the largest and smallest spheres, except for at selected values of $X^j$, it seems clear that the small spheres would move about as rattlers in the interstices formed by jammed larger spheres. It is interesting therefore that we have found that there are densest binary packings over the majority of the $\alpha - x$ plane that are composed of phases that do not include rattlers.

For the rectangular region $\alpha < 0.2, x > 11/12$, we have not attempted to identify densest
packings. This is because the number of distinct densest packings, for example, those of type $XY_n$, approaches infinity as $\alpha \to 0$ with $x \to 1$. In this latter limit, the densest packings are the $XY_\infty$ packings consisting of infinitesimally small Barlow-packed small spheres located within the spaces between Barlow-packed large spheres. The packing fraction of this packing is $\delta$,

$$\lim_{(\alpha,x) \to (0,1)} \phi_{\text{max}}(\alpha, x) = 1 - (1 - \pi/\sqrt{18})^2 = 0.932649 \ldots \quad (8)$$

At all points $(\alpha, x)$ outside of the rectangular region $\alpha < 0.2$, $x > 11/12$, we have identified putatively densest packings that consist only of periodic alloy phases. However, due to the infinity of densest Barlow packings (which are, in general, directionally periodic), all densest packings that contain a periodic monodisperse phase are degenerate in density with packings exhibiting an aperiodic monodisperse phase. Additionally, there are alloys that can be paired with monodisperse Barlow packings without a boundary cost, e.g., the AlB$_2$ alloy. This pairing allows a “mixed-phase” densest packing, or a densest packing composed of a single aperiodic (directionally periodic) phase. There are also pairs of alloys that appear to exhibit this property.

For the majority of the area in the $\alpha$-$x$ plane, the densest packings consist of two phase-separated phases, one alloy and one monodisperse. For $\alpha > \alpha^* \approx 0.660$, the known densest binary packings consist simply of two phase-separated monodisperse Barlow-packed phases. For $(\alpha, x) \in (0, \alpha^*) \times (0, 1)$, either a single alloy phase or a combination of an alloy and a monodisperse phase is known to be denser than two phase-separated monodisperse phases.

At certain points, densest packings consisting of three distinct phases can exist. Examples of this case include; at $\alpha = \alpha^*$, $0 < x < 1$, where two monodisperse phases and one A$_3$B phase exhibit packing fraction $\pi/\sqrt{18}$; at about $\alpha = 0.292$, $6/7 < x < 1$ where one monodisperse (small spheres), one (6-1)$_{10}$, and one (6-1)$_8$ phase exhibit a peak packing fraction of about 0.801; and at the same $\alpha$ with $1/2 < x < 6/7$ where one (6-1)$_{10}$, one (6-1)$_8$, and one XY phase exhibit a peak packing fraction of about 0.801. One example of a packing with four distinct phases occurs at about $\alpha = 0.480$, $1/2 < x < 2/3$, where one monodisperse (large spheres), one (7-3), one AuTe$_2$, and one (2-2)$^*$ phase exhibit a peak packing fraction of 0.748.
FIG. 6: (Color online) Putative densest packing ($\phi = 0.818$) at radius ratio $\alpha = 0.2195$ of 11 small spheres and 1 large sphere in a periodic fundamental cell. In this image, small spheres in tetrahedral interstices are shown in green (dark grey) and small spheres in octahedral interstices are shown in yellow (light grey). The fundamental cell of this (11-1) alloy belongs to the tetragonal lattice system.

B. Densest packings for $\alpha \leq \sqrt{2} - 1$

Many of the densest binary alloys for $\alpha < \sqrt{2} - 1$ are of the XY$_n$ type. In an XY$_n$ alloy, the small spheres, of which there are $n$ for every large sphere, are distributed in the octahedral and sometimes tetrahedral interstices, of which there are one and two, respectively, for each large sphere, of strictly jammed Barlow-packed large spheres. The XY$_n$ alloys are present in the densest binary packings that we have found for $n = 1, 2, 4, 8, 10$ and 11. In these packings, the small spheres occupy the interstices as rattlers, except for at “magic” [38] $\alpha$ where they are jammed between large spheres, e.g., at $\alpha = \sqrt{2} - 1$ for the NaCl alloy. All XY$_n$ alloys belong to the cubic lattice system.

For $n = 1, 2, 4$, and 8, these small spheres occupy only the octahedral interstice, where for $n = 4$ and $n = 8$, each set of 4 and 8 spheres in an interstice at the “magic” radii form a perfect tetrahedron and cube, respectively. For $n = 10$, a small sphere occupies each of the tetrahedral interstices, and at the magic radius the remainder form a perfect cube; for $n = 11$, there is one extra small sphere in the cube’s center. Additionally, for $n = 2, 4, 8$ and 10, there are XY$_n$ alloys for $\alpha$ greater than the magic radius ratios. These packings
FIG. 7: (Color online) Phase diagram in \((\alpha, x)\) for \(0 \leq \alpha \leq \sqrt{2} - 1\), excluding the region \(\alpha < 0.2\) and \(x > 11/12\), of the densest-known binary sphere packings in \(\mathbb{R}^3\) considering periodic packings with minimal bases of 12 or fewer spheres. This image is a blow-up of the left hand side of Fig. 5.

FIG. 8: (Color online) Putative densest packing \((\phi = 0.797)\) at radius ratio \(\alpha = 0.2503\) of 10 small spheres and 1 large sphere in a periodic fundamental cell. In this image, small spheres in tetrahedral interstices are shown in green (dark grey) and small spheres in octahedral interstices are shown in yellow (light grey). The (10-1) alloy belongs to the rhombohedral lattice system.

consist of large spheres arranged as in a Barlow packing (with cubic symmetry) but not in contact, with interstitial jammed small spheres arranged as was the case for the magic \(\alpha\).

In the case of \(XY_n\) packings where the large spheres are in contact, it is clear that there is no boundary cost between monodisperse layers of contacting spheres packed in a triangular
FIG. 9: (Color online) Putative densest packing \((\phi = 0.789)\) at radius ratio \(\alpha = 0.2781\) of six small spheres and one large sphere in a periodic fundamental cell. In this image, dotted lines between small spheres are drawn to indicate distances and do not indicate contacts. The (6-1)\textsubscript{10} alloy belongs to the orthorhombic lattice system.

lattice (which we recall is one layer of a Barlow packing) and an XY\textsubscript{n} packing. Furthermore, for \(x < n/(n+1)\), different numbers of small spheres can be distributed among the interstices of the Barlow-packed large spheres. Consequently, wherever a densest packing consists of any XY\textsubscript{n} phase and a Barlow-packed monodisperse phase of large spheres, mixed phase packings and aperiodic alloy phase packings are also densest packings.

The (11-1) and (10-1) alloys are similar to the XY\textsubscript{11} and XY\textsubscript{10} alloys, respectively, except that they belong to the tetragonal and rhombohedral lattice systems. The unit cells of these packings can be viewed respectively as “stretched” and “skewed” versions of the XY\textsubscript{11} and XY\textsubscript{10} unit cells, and the packings of large spheres can be seen this way as well. However, the clusters of contacting small spheres that occupy the octahedral interstices in these packings do not stretch and skew in the same fashion as the large spheres. Figures 6 and 8 are images that highlight the symmetry present in these alloys.

The (6-1)\textsubscript{10} alloy can be described as a body-centered orthorhombic packing of large spheres with four small spheres present on each of the faces. The small spheres on each face are not in contact, and they are not equidistant from one another owing to the different lengths of the three lattice vectors comprising the orthorhombic unit cell. Figure 9 illustrates the lack of contact between small spheres, in that the distances depicted between small spheres are all greater than \(2\alpha = 0.5562\) large sphere radii. In Fig. 9, the central large
FIG. 10: (Color online) Putative densest packing ($\phi = 0.799$) at radius ratio $\alpha = 0.2980$ of six small spheres and one large sphere in a periodic fundamental cell. In this image, dotted lines between small spheres are drawn to indicate distances and do not indicate contacts. The (6-1)$_8$ suballoy belongs to the triclinic lattice system.

sphere contacts all surrounding spheres and the central large spheres in the adjacent unit cells on the $z$-axis, where the $z$-axis is along the basis vectors that are 2.0000 sphere diameters in length.

The (6-1)$_8$, (6-1)$_6$, and (6-1)$_4$ suballoys are a subdivision of the alloy exhibiting triclinic lattice system characterization with six small and one large spheres in its minimal basis.

FIG. 11: (Color online) Putative densest packing ($\phi = 0.794$) at radius ratio $\alpha = 0.3151$ of six small spheres and one large sphere in a periodic fundamental cell. The (6-1)$_6$ suballoy belongs to the triclinic lattice system.
FIG. 12: (Color online) Putative densest packing ($\phi = 0.783$) at radius ratio $\alpha = 0.3293$ of six small spheres and one large sphere in a periodic fundamental cell. The (6-1)$_4$ suballoy belongs to the triclinic lattice system.

This alloy is present in the densest packings over the approximate range $0.292 \leq \alpha \leq 0.352$, and it is very similar to the (6-1)$_{10}$ alloy. Figures 10, 11, and 12 illustrate large-large and small-small sphere contacts in the (6-1)$_8$, (6-1)$_6$, and (6-1)$_4$ suballoys, respectively. The small spheres in the (6-1)$_8$ suballoy do not contact one another, though many of those in the (6-1)$_6$ and (6-1)$_4$ alloys do. Additionally, the centers of the small spheres in the (6-1)$_4$ alloy do not lie on the faces of the triclinic unit cell.

It is also the case that over the entire range that the (6-1) alloys are present in the densest packings, they can form mixed phase packings with large spheres packed as in a Barlow packing, or with large spheres packed as in a Barlow packing with one small sphere (a rattler) in the octahedral interstice. These mixed phase packings exhibit only slightly smaller packing fractions than their phase-separated counterparts. This is possible due to the nearly cubic symmetry of the (6-1) packings, which allows only a small boundary cost between a (6-1) unit cell and a Barlow-packed unit cell.

C. Densest packings for $\alpha > \sqrt{2} - 1$

The previously known densest alloys for $\alpha > \sqrt{2} - 1$ all exhibit ratios of small to large spheres of either one to one or two to one. Perhaps the best known is the AlB$_2$ alloy, Fig. 13 with two small and one large spheres in its minimal basis, present in the densest
FIG. 13: (Color online) Putative densest packing ($\phi = 0.7793$) at radius ratio $\alpha = 0.5500$ of two small spheres and one large sphere in a periodic fundamental cell. The AlB$_2$ alloy belongs to the hexagonal lattice system.

FIG. 14: (Color online) Phase diagram in ($\alpha, x$) for $\sqrt{2} \leq \alpha \leq 1$ of the densest-known binary sphere packings in $\mathbb{R}^3$ considering periodic packings with minimal bases of 12 or fewer spheres. This image is a blow-up of the right hand side of Fig. 5.

Packings over the range $\sqrt{7/3} - 1 \leq \alpha \leq 0.620$. This alloy phase can be described as alternating layers of contacting small spheres packed in a honeycomb lattice and large spheres packed in a triangular lattice. The alloy exhibits two maxima in packing density, one at
\[ \alpha = \sqrt{7/3} - 1 \] and the other at \( \alpha = 1/\sqrt{3} \), with \( \phi_{max}(\sqrt{7/3} - 1, 2/3) = 0.782112 \ldots \) and \( \phi_{max}(1/\sqrt{3}, 2/3) = 0.779205 \ldots \). At both maxima, the large spheres are in contact both parallel and perpendicular to the planes of the layers.

![Figure 15](image.png)

**FIG. 15:** (Color online) Putative densest packing (\( \phi = 0.759 \)) at radius ratio \( \alpha = 0.4597 \) of four small and two large spheres in a periodic fundamental cell. The HgBr\(_2\) alloy belongs to the orthorhombic lattice system.

The HgBr\(_2\) alloy was recently discovered to be present in the densest packings [37], a finding that our results support. The alloy phase belongs to the orthorhombic lattice system, and its minimal basis is composed of four small and two large spheres. It exhibits many local maxima and minima in packing fraction over the approximate range \( 0.443 \leq \alpha \leq 0.468 \) that it appears in the densest packings, suggesting that its contact network changes many times over this range. Due to these many local extrema, the packing fraction of the pure HgBr\(_2\) alloy phase does not vary much, with \( 0.752 \leq \phi_{max}(\alpha, 2/3) \leq 0.760 \) over the aforementioned range in \( \alpha \). Figure 15 highlights the large-large and small-small sphere contacts in the alloy.
at $\alpha = 0.4597$.

FIG. 16: (Color online) Putative densest packing ($\phi = 0.758$) at radius ratio $\alpha = 0.4995$ of two small spheres and one large sphere in a periodic fundamental cell. The fundamental cell of this AuTe$_2$ alloy belongs to the monoclinic lattice system.

The AuTe$_2$ alloy was also recently discovered to be present in the densest packings \cite{37}. The alloy phase belongs to the monoclinic lattice system, and its minimal basis is composed of two small spheres and one large sphere. In a previous work \cite{33}, our phase diagram indicated that this alloy was present in the densest packings over the approximate range $0.480 \leq \alpha \leq 0.528$, the same range that was reported in Ref. \cite{37}. However, we correct this statement to read that the alloy appears to be present in the densest packings over the range $0.488 \leq \alpha \leq 0.528$, with the (4-2) alloy present over the approximate range $0.480 \leq \alpha \leq 0.488$. Figure 16 highlights the large-large and small-small sphere contacts in the AuTe$_2$ alloy at $\alpha = 0.4995$.

The A$_3$B alloy was recently discovered \cite{36} to be the densest-known binary alloy over the approximate range $0.619 < \alpha < \alpha^*$. Previously, the AlB$_2$ alloy was thought to be the only alloy denser than phase-separated monodisperse small and large spheres for high enough $\alpha$, where it becomes less dense than a phase-separated monodisperse packing for all $\alpha > 0.623387 \ldots$. The fundamental cell of the A$_3$B alloy, depicted in Fig. 17, belongs to the orthorhombic lattice system, and it contains six small and two large spheres.

In our investigations, the (2-2)* alloy exhibits the same packing fraction (error of less than $10^{-4}$) as the “Structure 2” alloy described in Ref. \cite{39}, which has four small and four large spheres in its minimal basis. Within the error, we were unable to determine whether
FIG. 17: (Color online) Putative densest packing ($\phi = 0.746$) at radius ratio $\alpha = 0.643$ of six small and two large spheres in a periodic fundamental cell. The A$_3$B alloy belongs to the orthorhombic lattice system.

FIG. 18: (Color online) Putative densest packing ($\phi = 0.746$) at radius ratio $\alpha = 0.4881$ of two small and two large spheres in a periodic fundamental cell. The (2-2)$^*$ alloy belongs to the monoclinic lattice system.

doubling the minimal basis from four to eight spheres, just as increasing the minimal basis from four small and four large to six small and six large for the (6-6) alloy, results in an increased packing fraction. We suggest that it might result in an increase of less than $10^{-4}$ over the approximate range $0.480 \leq \alpha \leq 0.497$ that the alloy appears in the densest packings,
though we would need to run simulations at higher accuracy in order to confirm or reject this hypothesis. Figure 18 depicts the fundamental cell of the (2-2)* packing, which belongs to the monoclinic lattice system, at $\alpha = 0.4881$.

![Diagram of fundamental cell](image)

**FIG. 19**: (Color online) Putative densest packing ($\phi = 0.758$) at radius ratio $\alpha = 0.4483$ of six small and six large spheres in a periodic fundamental cell. The (6-6) alloy belongs to the triclinic lattice system.

The “Structure 1” alloy described in Ref. [39] has a minimal basis of four small and four large spheres. However, our simulations show that increasing the minimal basis to six small and six large spheres results in identification of a denser alloy. Specifically, we find (error of less than $10^{-4}$) that the (6-6) alloy exhibits the same packing fraction as the “Structure 1” alloy over the approximate range $0.414 \leq \alpha < 0.428$, and a denser packing fraction over the approximate range $0.428 \leq \alpha \leq 0.457$. The (6-6) alloy phase, illustrated in Fig. 19 belongs to the triclinic lattice system and is similar to a skewed and stretched version of the NaCl alloy. It is unclear if increasing the minimal basis beyond 12 spheres will result in a slightly denser alloy over the approximate range $0.414 \leq \alpha \leq 0.457$ that the (6-6) alloy appears to be present in the densest packings.

The (7-3) alloy appears in the densest packings over the approximate range $0.468 \leq \alpha \leq 0.480$. Its minimal basis contains seven small and three large spheres, and the alloy belongs to the orthorhombic lattice system. It exhibits a local maximum at $\phi_{max}(0.474568\ldots, 7/10) =$
0.752189 . . . For $\alpha < 0.474568$ where the alloy appears in the densest packings, it is stabilized along the $x$-axis and $y$-axis (the axes parallel to the basis vectors in Fig. 20 shown as having lengths 2.0 and 9.65, respectively) by large-large contacts, and along the $z$-axis it is stabilized by small-large contacts. For $\alpha > 0.474568$ . . . where the alloy appears in the densest packings, the $y$-axis is stabilized both by large-large and small-large contacts.

The (5-2) alloy belongs to the monoclinic lattice system and appears in the densest packings only over a very short range of $\alpha$, approximately $0.480 \leq \alpha \leq 0.483$. This brief appearance is not due to a local maximum in packing fraction in the (5-2) alloy, but rather to the fact that other dense binary alloys, such as the (4-2), HgBr$_2$, AuTe$_2$, and (7-3), all

FIG. 20: (Color online) Putative densest packing ($\phi = 0.752$) at radius ratio $\alpha = 0.4682$ of seven small and three large spheres in a periodic fundamental cell. The (7-3) alloy belongs to the orthorhombic lattice system.
happen to exhibit relatively lower packing fractions over this range of $\alpha$. One notable feature of the (5-2) alloy is a large void space, visible in Fig. 21 just above the four large spheres at the top right of the image.

The (4-2) alloy, illustrated in Fig. 22, is present in the densest packing over the approximate range $0.480 \leq \alpha \leq 0.488$. It has four small and two large spheres in its minimal basis and belongs to the triclinic lattice system. The alloy is very similar in packing fraction to both the AuTe$_2$ and HgBr$_2$ alloys over the range of $\alpha$ in which it appears in the densest packings. However, the (4-2) alloy fundamental cell has less symmetry, and the distortion in the cell away from a monoclinic arrangement allows for a slightly increased packing fraction over the range $0.480 \leq \alpha \leq 0.488$ as compared to the AuTe$_2$ alloy.
D. Another dense packing

The (8-1) alloy is particularly dense over the range $0.244 \leq \alpha \leq 0.253$, but it does not appear in the densest packings. As can be seen in Fig. 23, the (8-1) alloy consists of large spheres arranged in a unit cell belonging to the triclinic lattice system, with small spheres in the primary and secondary interstices. There are six small spheres arranged in a skewed octahedron in each primary interstice, and a small sphere in each secondary interstice, where there are twice as many secondary interstices as primary interstices. Interestingly, at
$x = 8/9$, the (8-1) alloy is denser than any phase-separated combination of a different alloy phase and a monodisperse phase. Nevertheless, a phase-separated combination of the (10-1) and XY$_4$ alloy phases permits a denser packing at $x = 8/9$ than a single (8-1) phase.

FIG. 23: (Color online) Very dense packing ($\phi = 0.787$) at radius ratio $\alpha = 0.2503$ of eight small and one large spheres in a periodic fundamental cell. This (8-1) alloy did not appear in the densest packings in our simulations; though it is denser over the approximate range $0.244 < \alpha < 0.253$ at $x = 8/9$ than the combination of two phase-separated phases where one is any other known alloy and the other is a monodisperse phase, the combination of two phase-separated alloy phases (the (10-1) and XY$_4$ phases) is denser. The (8-1) alloy belongs to the triclinic lattice system.

VI. CONCLUSIONS

We have surveyed the $\alpha$-$x$ plane at high resolution in both $\alpha$ and $x$ in order to find the densest binary sphere packings in $\mathbb{R}^d$ for minimal bases of up to 12 spheres. Employing an implementation of the TJ algorithm, we have identified all of the previously known alloys present in the densest packings and found many new alloys as well. We have described and presented the structure and symmetries of these densest alloys, and we have classified them by the composition of their minimal bases and lattice system characterization of their unit cells. Taken together, these results demonstrate that there is a broad diversity of alloys present in the densest packings, including alloys with large minimal bases and uncommon small to large sphere number ratios, e.g., the (6-6), (7-3) and (5-2) alloys.

We have also discussed the densest binary packings in $\mathbb{R}^3$, which are composed of phase-separated densest Barlow and alloy phases. We have proved that for any packing consisting
of $\eta$ different types of objects in $\mathbb{R}^d$, there is a densest packing that consists of no more than $\eta$ different phases. Additionally, we have discussed the properties of the function $\phi_{\text{max}}(\alpha, x)$ and described its features in the limit as $(\alpha, x) \to (0, 1)$.

One implication of our findings is that entropic (free-volume maximizing) particle interactions contribute to the structural diversity of mechanically stable and ground-state structures of atomic, molecular, and granular solids. Additionally, the structures we have identified can be useful as known points of departure when investigating experimentally the properties of binary solids composed of particles that exhibit steep isotropic pair-repulsion, including of dense atomic and molecular phases at high temperatures and pressures. In particular, some of the novel structures that we have identified could correspond to currently unidentified stable atomic and molecular states of matter. We note though that these novel structures would be most relevant to binary phases, perhaps at high temperatures and pressures, where the two particle-types exhibit roughly additive pair repulsion.

Though we have limited ourselves in this work to minimal bases of 12 or fewer spheres, the discovery of the (7-3), (6-6), and (5-2) alloys suggests that periodic structures with minimal bases larger than 12, further directionally-periodic, quasicrystalline and disordered structures might be present among the densest packings. This may also include a densest alloy, composed of a minimal basis of greater than 12 spheres, for $\alpha > \alpha^*$.

It is possible that the densest packings we have identified have a relation to the structures of glassy binary sphere solids and/or to those of binary sphere liquids near the freezing point. For example, recent work [55] demonstrates that a binary metallic glass, Ce$_{75}$Al$_{25}$ ($x = 1/4$, with the atomic volume of Ce about twice that of Al at ambient pressure), exhibiting long range structural order can be created by a melt-spinning process. Further investigation suggests that the long range fcc order is derived from the binary material’s densely packed configuration during spinning. It is possible that other binary glasses could exhibit similar long range order related to the densest packings of binary spheres at specified $(\alpha, x)$.

In future work, we will employ the TJ algorithm to study maximally random jammed (MRJ) packings of binary spheres at specified $(\alpha, x)$. This is a complicated problem, in part due to the difficulty in defining a MRJ state for binary packings. Nevertheless, a thorough investigation may reveal similarities between the MRJ packings and the densest binary packings at the same radius ratios $\alpha$ and small sphere relative concentrations $x$.  

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Appendix A: Implementation of the Algorithm

The implementation of the TJ algorithm for binary spheres requires a multistep process. This multistep process is run many times with many different initial configurations of spheres, in particular over initial configurations where the positions of large and small spheres are interchanged within a periodic unit cell.

In the first step of the process, an initial configuration of nonoverlapping small and large spheres is generated. This is accomplished through a random sequential addition process of adding large spheres to a randomly generated unit cell, then choosing which spheres will be designated small and which will be large. The cell is randomly generated in $\mathbb{R}^3$ using five random variables which represent the angles between the three lattice vectors and the relative lengths of the second and third lattice vectors to the first, which is normalized. The angles and lattice vector lengths are required to fall within certain bounds, and the total volume of the cell is bounded from below. These bounds are useful algorithmically in preventing overlap between the spheres in the unit cell and their images in non-adjacent unit cells.

The next step is to solve the linear programming problem (5) assuming that $\mathcal{R} = 0$, where we recall that $\mathcal{R}$ represents the higher order terms in the linear expansion of the packing problem and its constraints. After solving the problem (5), it is necessary to check if any overlap is present between spheres in the unit cell, or between the spheres in the unit cell and their images in surrounding cells. This step is necessary because $\mathcal{R}$ is sometimes negative, which can result in a solution to the problem (5) with overlap between spheres.
The higher order terms $R$ can be written,

$$R = 3\Delta r_{ij} \cdot \epsilon^2 \cdot \Delta r_{ij} + 2|\epsilon \cdot r_{ij} + \Delta r_{ij}|^2 - |\epsilon \cdot (r_{ij} - \Delta r_{ij})|^2 - |\Delta r_{ij} - \epsilon \cdot \Delta r_{ij}|^2. \quad (A1)$$

The first two terms in Eq. (A1) are positive semi-definite and the last two negative semi-definite. When the last two terms are greater in absolute value than the first two, this indicates that overlap between spheres can exist in a correctly-solved linearized programming problem.

If overlap is present between any two spheres, the lattice vectors $\{\lambda_i\}$ are resized by a constant such that all previously overlapping spheres are now out of contact by at least some small $\delta > 0$. All spheres in the packing are subsequently displaced in random directions by small random distances such that all distances are less than or equal to $\delta$. This step is necessary so that the algorithm does not become stuck in a loop. Additionally, the randomness introduced by this step aids in finding densest packings. If no overlap is present, then no resize of the lattice vectors is necessary. In either case, the algorithm repeats until there is no solution to the problem that reduces packing fraction, i.e., the packing is strictly jammed.

**Appendix B: Proof of Theorem 1**

To prove theorem 1, we will utilize the fundamental theorem of linear programming, which states that there is always a globally optimal solution to a linear programming problem (that has at least one solution) located at (at least) one of the vertices of the convex polytope that is the problem’s feasible region. In this case, the objective function of the linear programming problem is the denominator of Eq. (6), and the feasible region is defined by the constraints on the variables $x_i^{F_j}$ that result from conservation of particle numbers. We first outline these constraints, then apply the fundamental theorem of linear programming to prove that for a packing of $\eta$ different sphere sizes in $\mathbb{R}^d$, there is at least one densest packing composed of no more than $\eta$ phase-separated phases.

As the $X^{(j)}$ are relative fractions, $\sum_{j=1}^{\eta} X^{(j)} = 1$ and $X^{(j)} \geq 0$ for all $j$ due to conservation of particle numbers. For the same reason, summing up all the relative fractions $x_i^j$ of spheres
of type $j$ in each alloy type $i$, we have,

$$
\sum_{i=1}^{\beta} \frac{S^j_i}{S^i_F} x^F_i = X^{(j)}, \quad (B1)
$$

where we note that each term in the sum on the left hand side of Eqs. (B1) is equal to $x^j_i$. It follows from Eqs. (B1) and the nonnegativity of the $x^F_i$ that

$$
\frac{S^j_i}{S^i_F} x^F_i \leq X^{(j)}, \quad (B2)
$$

or for each phase $i$ and sphere type $j$, the relative fraction $x^j_i$ of spheres of type $j$ in phase $i$ is less than or equal to the total relative fraction of spheres $X^{(j)}$ of type $j$.

For each variable $x^F_i$, there is one or more indices $j$ with nonzero $S^j_i$ that yields the most restrictive constraint on $x^F_i$ from Eqs. (B2), i.e., one that yields the minimum value of $X^{(j)}/S^j_i$ from among all $j$. To be consistent with previous index nomenclature, we term this first such index $J_i$. Employing this form, the Eqs. (B2) reduce to $\beta$ inequalities that together with the nonnegativity of the $x^F_i$ produce the $\beta$ bounds,

$$
0 \leq x^F_i \leq \frac{S^F_i}{S^j_i} X^{(J_i)}, \quad (B3)
$$

which describe a hyper-rectangular prism in $\beta$-dimensional Euclidean space in the variables $x^F_i$.

The $\eta$ equations (B1) describe $\eta$ hyperplanes in $\beta$-dimensional Euclidean space. The convex polytope that forms the feasible region consists of their intersection with each other and the hyper-rectangular prism described by inequalities (B3). We can thus formulate a linear programming problem corresponding to the maximum of Eq. (6) as,

$$
\min \sum_{i=1}^{\beta} \frac{C_i}{S^F_i} x^F_i, \quad (B4)
$$

subject to the equality constraints (B1) and the inequality constraints (B3). This allows us to prove Theorem 1, as follows.

\textit{Proof.} Due to the monodisperse alloys, the hyperplanes defined by Eqs. (B1) have at least
one point of mutual intersection. Terming the relative relative fractions of the monodisperse alloys $x_1^1 \ldots x_\eta^\eta$, this point is $\{x_1^1 \ldots x_\eta^\eta\} = \{X^{(1)} \ldots X^{(\eta)}\}$ and $\{x_i^{F_i} = 0; \ i > \eta\}$, namely the packing where all phases are monodisperse. As this point is contained within the feasible region, we can apply the fundamental theorem of linear programming to state that there is a globally optimal solution to the problem (B4) located at (at least) one of the vertices of the convex polytope formed by the intersection of the $\eta$ hyperplanes described by Eqs. (B1) and the hyper-rectangular prism described by inequalities (B3).

To prove that there is a globally optimal solution that consists of no more than $\eta$ phase-separated phases, we will show that there can be no more than $\eta$ positive values of $x_i^{F_i}$ at any of the vertices of the feasible region. To this end, we will first describe the vertices of the feasible region where the $\eta$ hyperplanes intersect the hyper-rectangular prism only at the lower bounds of inequalities (B3). Immediately following, we will describe the vertices when the $\eta$ hyperplanes intersect at one or more of the upper bounds of inequalities (B3).

The vertices where the $\eta$ hyperplanes intersect only at the lower bounds of the hyper-rectangular prism consist of all combinations of no more than $\eta$ positive $x_i^{F_i}$ and no fewer than $\beta - \eta$ zero values of $x_i^{F_i}$ such that Eqs. (B1) are satisfied. There can be no more than $\eta$ nonzero $x_i^{F_i}$ at a vertex because the vertices must occur where at least $\beta$ equality constraints are satisfied, i.e., where $x_i^{F_i} = 0$ on at least $\beta - \eta$ of the halfplanes described by the inequalities (B3), and at the intersection of the $\eta$ hyperplanes described by Eqs. (B1). There can be fewer than $\eta$ positive $x_i^{F_i}$, in particular if the intersection of the $\eta d$-dimensional hyperplanes describes a hyperplane embedded in $\beta$ dimensions that is more than $(\beta - \eta)$-dimensional, or if one of the $\eta$ hyperplanes happens to intersect with the halfplane described by one of the lower bounds of the inequalities (B3) at a given vertex where all nonzero $x_i^{F_i}$ are positive.

If the intersection of the $\eta$ hyperplanes simultaneously intersects $t$ faces of the hyper-rectangular prism at the upper bounds of inequalities (B3), then for a set of $t$ indices $\{q\}_t$, $x_q^{F_q} = (S_q^{F_q}/S_q^{J_q})X^{(J_q)}$. At all points contained within this intersection, all spheres of types $J_q$ are present only in their respective phases $q$. This means that for all other $x_i^{F_i}$ where phase $i$ includes any spheres of types $J_q$, $x_i^{F_i} = 0$. Excluding these phases and the phases $\{q\}_t$, the problem is reduced to the remaining $\beta_t$ variables with indices $\{i\}_t$ in $\beta_t$ dimensions,
and where there are \( \eta - t \) constraints of the form,

\[
\sum_{\{i\}_t} \frac{S^j_i}{S_{F_i}} x_{F_i} = X^{(j)} - \sum_{\{q\}_t} \frac{S^j_q}{S_{F_q}} x_{F_q}.
\]

(B5)

In the Eqs. (B5), the index \( j \) is for all \( j = 1 \ldots \eta \) excluding the \( j = \{J_q\} \), the sum on the left hand side runs over the \( \beta_t \) indices included in the set \( \{i\}_t \), and the sum on the right hand side runs over the \( t \) indices included in the set \( \{q\}_t \).

In this reduced case, the Eqs. (B5) imply new upper bounds on the \( \beta_t \) remaining \( x_{F_i} \) which describe a new hyper-rectangular prism in \( \beta_t \) variables. However, the lower bounds on the \( \beta_t \) variables \( x_{F_i} \) over the indices \( \{i\}_t \) are the same; consequently, the vertices of the feasible region where the \( \eta - t \) hyperplanes described by Eqs. (B5) intersect the reduced hyper-rectangular prism only at its lower bounds include no more than \( \eta - t \) positive \( x_{F_i} \) and no fewer than \( \beta_t - \eta + t \) zero values of the remaining \( x_{F_i} \). Coupled with the \( \beta - \beta_t - t \) zero values of \( x_{F_i} \) that include spheres of types \( J_q \) and the \( t \) values \( x_{F_q} = (S_{F_q}/S_{J_q})X^{(J_q)} \), this gives no more than \( \eta \) positive \( x_{F_i} \) and no fewer than \( \beta - \eta \) zero values of \( x_{F_i} \).

The value \( t \) cannot exceed \( \eta \) because at \( t = \eta \), \( \beta_t = 0 \), as all phases must include at least one type of sphere. It follows that all vertices must include between \( t = 0 \) and \( t = \eta \) intersections at the upper bounds of the hyper-rectangular prism, and so we have proved that there cannot be more than \( \eta \) positive \( x_{F_i} \) at any vertex. It follows directly, since there is at least one global optimum on a vertex, that there is always at least one densest packing that includes no more than \( \eta \) phase-separated phases.

Appendix C: Packing Fractions

The packing fractions in this Appendix are for the periodic alloys that comprise the densest packings at given values of \( \alpha \). By comparing the alloys found by the algorithm
to densest alloys for which we have explicit representations of the packing fraction, we have discovered that the packing fractions are in general about $1.0 \times 10^{-4}$ too low, though sometimes as much as $2.5 \times 10^{-4}$ too low. For this reason, and due to the resolution of our survey in $\alpha$, we report packing fractions only to the third decimal place. Additionally, we note that our algorithm, being constructive, always produces packing fractions for real packings, and therefore the fractions presented are all lower bounds on the true maximal fractions. Finally, we note that although the comparisons we have made in the text to explicitly-known packing fractions are for the precise values of $\alpha$ that we employed in our survey, the values of $\alpha$ reported in this table have been rounded to the third decimal place.

TABLE I: Selected densest binary alloy packing fractions.

| $\alpha$ | (11-1) | (10-1) | (6-1)$_{10}$ | (6-1)$_{4,6,8}$ | $\alpha$ | (6-6) | (7-3) | (5-2) | (4-2) | (2-2)* |
|----------|--------|--------|--------------|----------------|----------|-------|-------|-------|-------|-------|
| 0.217    | 0.823  |        |              |                | 0.414    | 0.793 |       |       |       |       |
| 0.220    | 0.818  |        |              |                | 0.417    | 0.789 |       |       |       |       |
| ...      |        |        |              |                | 0.420    | 0.786 |       |       |       |       |
| 0.225    | 0.825  |        |              |                | 0.423    | 0.783 |       |       |       |       |
| 0.228    | 0.822  |        |              |                | 0.426    | 0.779 |       |       |       |       |
| 0.230    | 0.820  |        |              |                | 0.428    | 0.776 |       |       |       |       |
| 0.233    | 0.818  |        |              |                | 0.431    | 0.773 |       |       |       |       |
| ...      |        |        |              |                | 0.434    | 0.771 |       |       |       |       |
| 0.245    | 0.804  |        |              |                | 0.437    | 0.768 |       |       |       |       |
| 0.247    | 0.800  |        |              |                | 0.440    | 0.765 |       |       |       |       |
| 0.250    | 0.797  |        |              |                | 0.443    | 0.763 |       |       |       |       |
| 0.253    | 0.794  |        |              |                | 0.445    | 0.760 |       |       |       |       |
| 0.256    | 0.791  |        |              |                | 0.448    | 0.758 |       |       |       |       |
| 0.258    | 0.789  |        |              |                | 0.451    | 0.756 |       |       |       |       |
| 0.261    | 0.787  |        |              |                | 0.454    | 0.754 |       |       |       |       |
| 0.264    | 0.785  | 0.781  |              |                | 0.457    | 0.751 |       |       |       |       |
| 0.267    | 0.783  | 0.782  |              |                | 0.460    |       |       |       |       |       |
| $\alpha$ | (11-1) | (10-1) | (6-1)$_{10}$ | (6-1)$_{8,6,4}$ | $\alpha$ | (6-6) | (7-3) | (5-2) | (4-2) | (2-2)$^*$ |
|-------|-------|-------|-------------|-------------|-------|-------|-------|-------|-------|---------|
| 0.270 | 0.781 | 0.784 |            |             | 0.463 |       |       |       |       |         |
| 0.273 | 0.785 |       |             |             | 0.465 |       |       |       |       |         |
| 0.275 | 0.787 |       |             |             | 0.468 | 0.752 |       |       |       |         |
| 0.278 | 0.789 |       |             |             | 0.471 | 0.752 |       |       |       |         |
| 0.281 | 0.792 |       |             |             | 0.474 | 0.752 |       |       |       |         |
| 0.284 | 0.794 |       |             |             | 0.477 | 0.750 |       |       |       |         |
| 0.287 | 0.797 |       |             |             | 0.480 | 0.748 | 0.746 | 0.744 | 0.744 |         |
| 0.289 | 0.800 |       |             |             | 0.483 |       | 0.746 | 0.746 | 0.744 |         |
| 0.292 | 0.801 |       |             |             | 0.485 |       |       | 0.748 | 0.745 |         |
| 0.295 |       | 0.800 |             |             | 0.488 |       |       | 0.750 | 0.746 |         |
| 0.298 |       | 0.799 |             |             | 0.491 |       |       |       | 0.747 |         |
| 0.301 |       | 0.798 |             |             | 0.494 |       |       |       |       | 0.748 |
| 0.304 |       | 0.797 |             |             | 0.497 |       |       |       |       | 0.749 |
| 0.307 |       |       |             |             | 0.797 |       |       |       |       |         |
| 0.309 |       |       |             |             | 0.796 |       |       |       |       |         |
| 0.312 |       |       |             |             | 0.795 |       |       |       |       |         |
| 0.315 |       |       |             |             | 0.794 |       |       |       |       |         |
| 0.318 |       |       |             |             | 0.793 |       |       |       |       |         |
| 0.321 |       |       |             |             | 0.792 |       |       |       |       |         |
| 0.324 |       |       |             |             | 0.788 |       |       |       |       |         |
| 0.326 |       |       |             |             | 0.786 |       |       |       |       |         |
| 0.329 |       |       |             |             | 0.783 |       |       |       |       |         |
| 0.332 |       |       |             |             | 0.780 |       |       |       |       |         |
| 0.335 |       |       |             |             | 0.778 |       |       |       |       |         |
| 0.338 |       |       |             |             | 0.775 |       |       |       |       |         |
| 0.341 |       |       |             |             | 0.773 |       |       |       |       |         |
| 0.343 |       |       |             |             | 0.771 |       |       |       |       |         |
| 0.346 |       |       |             |             | 0.769 |       |       |       |       |         |
continued from previous page

\[
\begin{array}{cccc|cccc}
\alpha & (11-1) & (10-1) & (6-1)_{10} & (6-1)_{8,6,4} & \alpha & (6-6) & (7-3) & (5-2) & (4-2) & (2-2)^* \\
0.349 & & & & & 0.768 & & & & & \\
0.352 & & & & & 0.766 & & & & & \\
\end{array}
\]

[1] S. Torquato and F. H. Stillinger, Rev. Mod. Phys. 82, 2633 (2010).
[2] G. L. Pollack, Rev. Mod. Phys. 36, 748 (1964).
[3] J. V. Sanders, Phil. Mag. A 42, 705 (1980).
[4] P. Bartlett, R. H. Ottewill, and P. N. Pusey, Phys. Rev. Lett. 68, 3801 (1992).
[5] M. J. Vlot, H. E. A. Huitema, A. de Vooys, and J. P. van der Eerden, J. Chem. Phys. 107, 4345 (1997).
[6] T. F. Middleton, J. Hernandez-Rojas, P. N. Mortenson, and D. J. Wales, Phys. Rev. B 64, 184201 (2001).
[7] M. Amsler and S. Goedecker, J. Chem. Phys. 133, 224104 (2010).
[8] S. Torquato, Random Heterogeneous Materials (Springer-Verlag, New York, 2002).
[9] P. M. Chaikin and T. C. Lubensky, Principles of Condensed Matter Physics (Cambridge University Press, Cambridge, 1995).
[10] J. P. Hansen and I. R. McDonald, Theory of Simple Liquids, 3rd ed. (Academic Press, Amsterdam, 2006).
[11] R. Zallen, The Physics of Amorphous Solids (John Wiley and Sons, New York, 1983).
[12] A. B. Hopkins, F. H. Stillinger, and S. Torquato, Phys. Rev. E 79, 031123 (2009).
[13] A. B. Hopkins, F. H. Stillinger, and S. Torquato, J. Math. Phys. 51, 043302 (2010); Phys. Rev. E 81, 041305 (2010); Phys. Rev. E 83, 011304 (2011).
[14] A. Donev, F. H. Stillinger, P. Chaikin, and S. Torquato, Phys. Rev. Lett. 92, 255506 (2004).
[15] Y. Jiao, F. H. Stillinger, and S. Torquato, Phys. Rev. E 79, 041309 (2009); R. D. Batten, F. H. Stillinger, and S. Torquato, Phys. Rev. E 81, 061105 (2010).
[16] S. Torquato and Y. Jiao, Nature 460, 876 (2009); Phys. Rev E 80, 041104 (2009); Phys. Rev. E 81, 041310 (2010).
[17] E. Chen, Disc. Comp. Geom. 40, 214 (2008); E. Chen, M. Engel, and S. Glotzer, Disc. Comp. Geom. 44, 253 (2010).
[18] Y. Kallus, V. Elser, and S. Gravel, Disc. Comp. Geom. 44, 245 (2010).
[19] J. de Graaf, R. van Roij, and M. Dijkstra, Phys. Rev. Lett. 107, 155501 (2011).
[20] Y. Jiao and S. Torquato, Phys. Rev. E 84, 041309 (2011).
[21] F. Ding and N. V. Dokholyan, Trends in Biotech. 23, 450 (2005); N. V. Dokholyan, Curr. Opin. Struct. Bio. 16, 79 (2006); C. H. Davis, H. Nie, and N. V. Dokholyan, Phys. Rev. E 75, 051921 (2007).
[22] D. Drasdo and S. Höhme, Phys. Bio. 2, 133 (2005).
[23] J. L. Gevertz, G. Gillies, and S. Torquato, Phys. Bio. 5, 036010 (2008); J. L. Gevertz and S. Torquato, PLoS Comp. Bio. 4, e1000152 (2008).
[24] G. M. Knott, T. L. Jackson, and J. Buckmaster, AIAA J. 39, 678 (2001); S. Kochevets, J. Buckmaster, T. L. Jackson, and A. Hegab, J. Prop. Pow. 17, 883 (2001); F. Maggi, S. Stafford, T. L. Jackson, and J. Buckmaster, Phys. Rev. E 77, 046107 (2008).
[25] M. Kolonko, S. Raschdorf, and D. Wäsch, Gran. Matt. 12, 629 (2010).
[26] W. Hume-Rothery, R. E. Smallman, and C. W. Haworth, The Structure of Metals and Alloys, 5th ed. (Metals and Metallurgy Trust, London, 1969).
[27] M. J. Murray and J. V. Sanders, Phil. Mag. A 42, 721 (1980).
[28] S. K. Sikka, Y. K. Vohra, and R. Chidambaram, Prog. Mat. Sci. 27, 245 (1982).
[29] A. R. Denton and N. W. Ashcroft, Phys. Rev. A 42, 7312 (1990).
[30] M. D. Eldridge, P. A. Madden, and D. Frenkel, Nature 365, 35 (1993); Mol. Phys. 79, 105 (1993); Mol. Phys. 80, 987 (1993).
[31] X. Cottin and P. A. Monson, J. Chem. Phys. 99, 8914 (1993); J. Chem. Phys. 102, 3354 (1995).
[32] M. Widom and M. Mihalkovic, J. Mater. Res. 20, 237 (2005).
[33] A. B. Hopkins, Y. Jiao, F. H. Stillinger, and S. Torquato, Phys. Rev. Lett. 107, 125501 (2011).
[34] S. Torquato and Y. Jiao, Phys. Rev. E 82, 061302 (2010).
[35] K. Y. Szeto and J. Villain, Phys. Rev. B 36, 4715 (1987).
[36] P. I. O’Toole and T. S. Hudson, J. Phys. Chem. C 115, 19037 (2011).
[37] L. Filion and M. Dijkstra, Phys. Rev. E 79, 046714 (2009).
[38] C. N. Likos and C. L. Henley, Phil. Mag. B 68, 85 (1993).
[39] G. W. Marshall and T. S. Hudson, Contr. Alg. Geo. 51, 337 (2010).
[40] R. Demchyna, S. Leoni, H. Rosner, and U. Schwarz, Z. Kristallogr. 221, 420 (2006).
[41] C. Cazorla, D. Errandonea, and E. Sola, Phys. Rev. B 80, 064105 (2009).

[42] V. Degtyareva, J. Synchrotron Rad. 12, 584 (2005).

[43] T. C. Hales, Ann. Math. 162, 1065 (2005).

[44] W. Barlow, Nature 29, 186 (1883).

[45] T. S. Hudson and P. Harrowell, J. Phys. Chem. B 112, 8139 (2008).

[46] J. K. Kummerfeld, T. S. Hudson, and P. Harrowell, J. Phys. Chem. B 112, 10773 (2008).

[47] L. Filion, M. Marechal, B. van Oorschot, D. Pelt, F. Smullenburg, and M. Dijkstra, Phys. Rev. Lett. 103, 188302 (2009).

[48] L. Bindi, P. J. Steinhardt, N. Yao, and P. J. Lu, Science 324, 1306 (2009).

[49] D. Levine and P. J. Steinhardt, Phys. Rev. B 34, 596 (1986).

[50] L. F. Toth, Regular Figures (Macmillan, New York, 1964).

[51] P. W. Leung, C. L. Henley, and G. V. Chester, Phys. Rev. B 39, 446 (1989).

[52] M. Widom, Phys. Rev. Lett. 70, 2094 (1993).

[53] S. Torquato, T. M. Truskett, and P. G. Debenedetti, Phys. Rev. Lett. 84, 2064 (2000); S. Torquato and F. H. Stillinger, J. Phys. Chem B 105, 11849 (2001).

[54] L. Filion, M. Hermes, R. Ni, E. C. M. Vermolen, A. Kuijk, C. G. Christova, J. C. P. Stiefelhagen, T. Vissers, A. van Blaaderen, and M. Dijkstra, Phys. Rev. Lett. 107, 168302 (2011).

[55] Q. Zeng et al., Science 332, 1404 (2011).