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The Densest Packing of AB Binary Hard-Sphere Homogeneous Compounds across all Size Ratios

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This paper considers the homogeneous packing of binary hard spheres in an equimolar stoichiometry, and postulates the densest packing at each sphere size ratio. Monte Carlo simulated annealing optimizations are seeded with all known atomic inorganic crystal structures, and the search is performed within the degrees of freedom associated with each homogeneous AB structure type. Structures isopointal to the FeB structure type are found to have the highest packing fraction at all sphere size ratios. The optimized structures match or improve on the best previously demonstrated packings of this type, and show that compound structures can pack more densely than segregated close-packed structures at all radius ratios less than 0.62.

Introduction

The packing of objects in space represents a fundamental constraint of the natural world and one of its most ubiquitous ordering principles. Both of these aspects of packing are central to the fields of intermetallic materials,[1,2] granular materials,[3] nanoparticle self-assemblies,[4,5] including those of geological[6] and biological[7] origin, and liquid crystals.[8] That a face-centered cubic (fcc) lattice is the densest packing of spheres in 3D has finally been rigorously established,[9,10] verifying that a simple lattice ordering arises from the infinite space of possibilities when structureless particles are subjected to nothing more than a maximal condition on density. What structures arise from this single condition when the objects being packed become more complex? Mixtures of spheres of two different sizes represent a simple increase in the complexity of the packed objects while exploring the structural variety provided by a smoothly varying size ratio.

It is the need to search over the space of structures in which packing problems find their most fundamental connection with the wide variety of natural phenomena. Most packing studies either select some structures to study[6,11−13] or carry out a statistical search in the space of structures.[5,14] Each technique explores only a small subset of the possible structures. In this study we have considerably extended the range of our search by using the extensive database of crystal studies to provide the set of starting crystal structures to be subsequently optimized for density. We optimize all of the common homogeneous equimolar structure types, and find that structures isopointal[15] to the FeB structure type have the highest packing fraction compared to all observed inorganic equimolar binary atomic compounds at all sphere size ratios. In addition to significantly improving on some of the best previously demonstrated packings, these results indicate that the space of compact packings occupies a restricted subdomain of the space of structures.

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Methods

Optimizations were performed on each homogeneous structure type occurring more than once among the 3000 full-occupancy crystal structures with AB stoichiometry recorded in the Inorganic Crystal Structure Database (ICSD).[16,17] By homogeneous, we mean that every particle of each type has the same environment, except for possible rotations. Up to 12 variable parameters in each structure type were determined automatically from the diversity of structures of that type in the database, after removing any structures using a different coordinate system or different Wyckoff sites. For each structure type, the packing fraction, φ, at each radius ratio, $\gamma = r_A/r_B$, was maximized by a simulated annealing algorithm, varying all particle coordinates and cell parameters under the constraint that the structure remains isopointal to the original structure type. The packing fraction, φ, of a structure is defined as the fraction of the total space occupied by the particles. Two hundred radius ratios between 0.005 and 1.000 were tested for each structure. Local optimizations that allowed variation of the radius ratio were also performed in the vicinity of any peak found.

The following paragraphs provide details of the density maximization algorithm. Readers not interested in the details can go straight to the results section. Simulated annealing is a stochastic optimization technique where a fitness function (the "energy", E) is minimized. The "temperature", T, of the algorithm which governs the likelihood, P, of accepting a Monte Carlo step, which increases the energy (according to the usual Metropolis criteria given in equation 1), is gradually reduced to 0 in order to bring the simulation toward the global energy minimum. The effective "energy" used for our optimization is given in equation 2. The configuration at which this function is minimized is identical to the configuration at which the packing fraction is maximized. Any function with this property has the same global optimum, and the arbitrary choice of energy function is simply to make convergence fast and robust. In this case, the asymptotic second term was added to prevent the early

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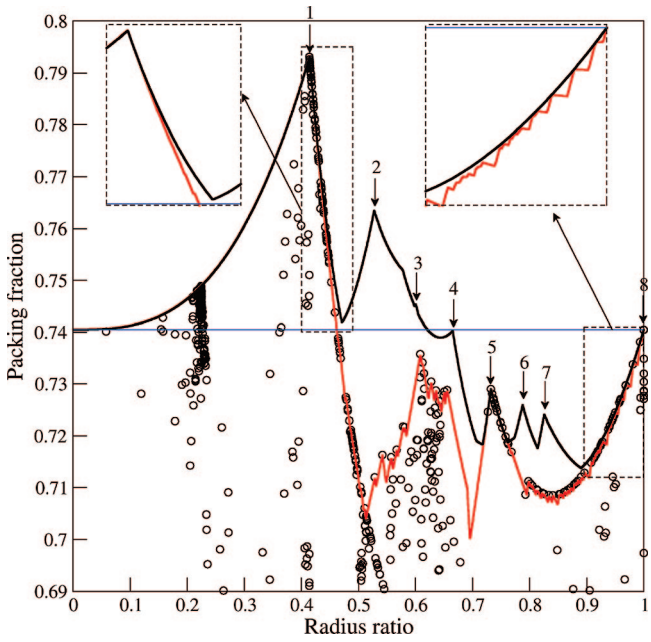


Figure 1. A comparison of optimized packing fractions to those displayed by atomic crystal structures. Black circles: the packing fraction at the optimized radius ratio for atomic crystal structures in the ICSD. Red line: the maximum packing fraction at all radius ratios obtainable by atomic crystal structures. Black line: the maximum packing fractions of Monte Carlo optimized structure types. Horizontal blue line: the packing fraction of single component (segregated) close-packed phases. Insets show that our optimization improves on the natural structures even at radius ratios where densely packed natural structures are common.

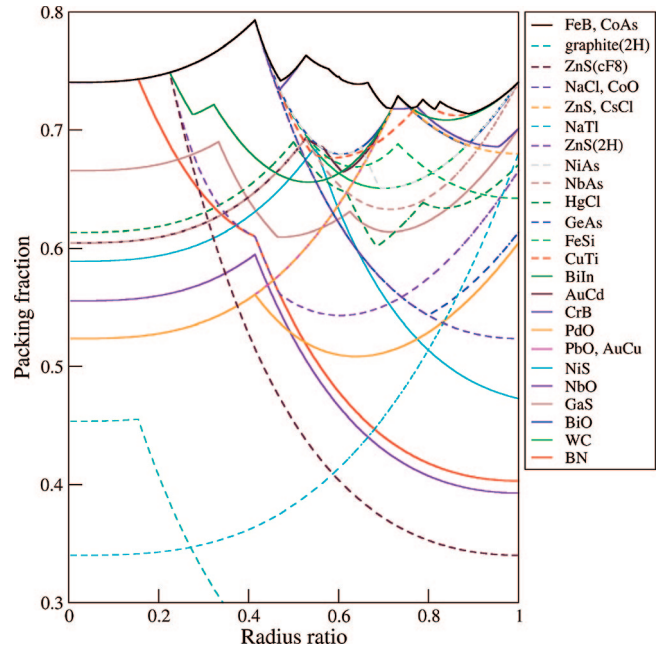


Figure 2. The space-filling curves of each homogeneous structure type, optimized at all radius ratios. Some nonisopointal structure types optimize to identical space-filling curves, usually when one adopts parameters that increase its symmetry at all radius ratios.

stages of the search from dwelling near $\varphi = 0$, where the density of states becomes infinite.

$$P = \exp\left(-\frac{\Delta E}{T}\right) \tag{1}$$

$$E = -\phi + \frac{0.2}{\phi} \tag{2}$$

Two types of annealing were performed: one starting at a high "temperature" of 0.6, began from typical coordinates from a crystal of that structure type, and was repeated 20 times using different random seeds; the other, a local optimization, started with a low temperature of 0.006, began from coordinates optimized at the previous or subsequent radius ratio, and was repeated 10 times from both directions. In each case, the size of the Monte Carlo steps was varied adaptively to give an acceptance rate of around 50% at all temperatures. The temperature was reduced at a rate no faster than 0.5% per 100 attempts, and the simulation was continued until the convergence of four decimal places in the packing fraction. At each radius ratio, the results of the best simulation were selected. The outcomes of the 40 simulations, which regularly matched the optimal value, indicate that these results are robust. However, it is always possible that the search did not find the global maximum if it occurs in a small region of configuration space or one separated by a high barrier.

Results and Discussion

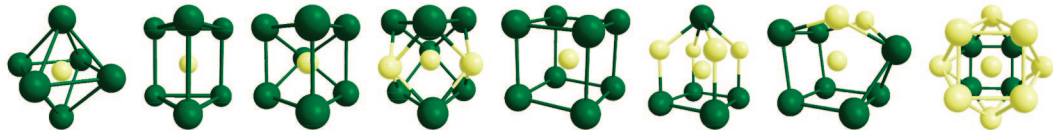
The upper envelope of maximized packing fractions among all structure types is recorded in Figure 1 as the black line. For comparison, we have optimized the packing fraction of every natural crystal structure with AB stoichiometry (but not necessarily homogeneous) by varying only the radius ratio of two different sized hard spheres placed at the A and B sites. In this case, the density is optimized, not over the space of particle coordinates as these are held fixed, but only over the one-dimensional space of the radius ratio. The value of γ and the associated maximum value of φ are plotted as circles in Figure 1. At each radius ratio, the upper envelope (red line) of the resulting scatter plot represents the best AB binary packings directly obtainable from the crystallographic database.

Figure 2 shows the individual space-filling curves for each of the structure types we analyzed. The FeB structure type is shown to be flexible enough to match or exceed the packing fraction of every other structure type at every radius ratio. In particular, we find that even close to radius ratios of 0.4142 and 1.0, respectively, the optimal structures exhibit a deviation away from what can be obtained from the native structures (see Figure 1 insets). Table 1 gives features of the structures occurring at the eight peaks of the optimized FeB curve (the Supporting Information gives the values of the free parameters required to construct these structures). The first (NaCl), second, fifth (CsCl), and eighth (decorated fcc) peaks can be generated using honeycombs of regular-faced polyhedra of large particles, with small particles filling the interstices of the largest polyhedra.[12] The remaining structures (3, 4, 6, and 7) do not conform to the single component polyhedral coordination shell implicit in the convex honeycombs.

The second, third, fourth, sixth, and seventh peaks are conspicuous by the absence of any points from the database, and thus do not conform to any known crystal structure (something of a triumph for a search that was based on known crystal structures). Why nature has not made full use of these efficient packings is an interesting question.

Over the range $0 < \gamma < 0.62...$, the optimized structure achieves a packing density greater than that of the fcc structure. This confirms a postulate that, without constraints on the stoichiometry, structures would achieve this over this

TABLE 1: The Structural Features of Local Maxima in the Packing Fraction as a Function of Radius Ratio (the Smaller Particles Are Labeled A, the Larger Particles Are Labeled B)

size ratio: γ	0.4142	0.5275	0.6005	0.6652	0.7321	0.7877	0.8255	1
packing fraction: φ	0.7931	0.7634	0.7454	0.7402	0.7290	0.7259	0.7241	0.7405
A contacts	6B	6B	7B	2A 7B	8B	4A 5B	2A 7B	8A 4B
B contacts	6A 12B	6A 10B	7A 8B	7A 6B	8A 6B	5A 8B	7A 6B	4A 8B
description	NaCl (fcc with octahedral holes filled)	closed triangular prisms layered then stacked	mono-capped open triangular prisms	tri-capped stretched triangular prisms	CsCl (simple cubic lattice with holes filled)	CuTi-like layered structure	distorted hexagonal tubes of B particles, enclosing zigzag chains of A particles	a decorated fcc lattice
particle A coordination shell								

same range.[6,18,19] Two of the peaks, the second and third, are in this range where densities are greater than that of the fcc structure. The fourth peak also comes very close but at a significantly higher radius ratio. The second peak, with a packing density of 0.7634, consists of small particles inside equilateral triangular prisms of large particles, which form face-sharing layers, with surfaces consisting of square lattices of large particles. These layers are offset and packed into an extended structure. It is structurally similar to chromium boride, but the natural structure and other similar structures (some at different stoichiometries) consistently show either stretched or compressed prisms,[20] giving a packing fraction lower than that of equilateral triangular prisms. The third peak, almost hidden by the shoulder of the second, is notable for its 7-fold coordination. The small particle is surrounded by a monocapped triangular prism of large particles. Again these prisms share faces to form the crystal. The fourth peak continues this structural theme, with each prism being stretched so that it is now equatorially tricapped with one large particle and two small particles. This structure matches one found using genetic algorithms applied to fused spheres.[5]

At every radius ratio, our solutions can also be considered optimized packings of fused spheres (heteroatomic touching-hard-sphere dimers). To achieve this at small radius ratios, the small particles must be displaced until they touch a large particle. For radius ratios between $\gamma = 0.4142$ and 1, every small particle is in contact with at least one large particle, and every large particle is in contact with at least one small particle. This, together with the homogeneity of the FeB structure type ensures that the sphere structures can be decorated with one contact bond per pair of particles, producing structures of packed dimers.

Conclusions

In this paper, we have greatly expanded the space of structures over which the density optimization is carried out in comparison to previous studies. A corresponding increase in the number of high density packing structures identified would not have been surprising. In looking further ahead, however, we also hope to better discern any geometrical "theme" that links our optimal packings. Our results provide an interesting amalgam of these expectations. There is a rich variation in structural maxima, with only small ranges over which continuous distortions alter the structure, before a discontinuous transformation occurs. There is, however, a surprisingly restricted space of maximum density packings, given that they all have at least the same symmetry operations as FeB, and the same site occupancy.

The specific structures obtained in this study can be considered as candidates when predicting phase diagrams of spherical or dimer particles.[21,22] Self-assembly into dense structures is often favored on entropic grounds, so these particular geometries may prove technologically useful in the construction of novel nanostructures.[4,5]

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Supporting Information Available: Full tables of crystallographic parameters (numerical values and exact expressions) for each of the peak structures. This material is available free of charge via the Internet at http://pubs.acs.org.

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