

Controlling the Short-Range Order and Packing Densities of Many-Particle Systems[†]

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Questions surrounding the spatial disposition of particles in various condensed-matter systems continue to pose many theoretical challenges. This paper explores the geometric availability of amorphous many-particle configurations that conform to a given pair correlation function $g(r)$. Such a study is required to observe the basic constraints of non-negativity for $g(r)$ as well as for its structure factor $S(k)$. The hard sphere case receives special attention, to help identify what qualitative features play significant roles in determining upper limits to maximum amorphous packing densities. For that purpose, a five-parameter test family of g 's has been considered, which incorporates the known features of core exclusion, contact pairs, and damped oscillatory short-range order beyond contact. Numerical optimization over this five-parameter set produces a maximum-packing value for the fraction of covered volume, and about 5.8 for the mean contact number, both of which are within the range of previous experimental and simulational packing results. However, the corresponding maximum-density $g(r)$ and $S(k)$ display some unexpected characteristics. These include absence of any pairs at about 1.4 times the sphere collision diameter, and a surprisingly large magnitude for $S(k=0)$, the measure of macroscopic-distance-scale density variations. On the basis of these results, we conclude that restoration of more subtle features to the test-function family of g 's (i.e., a split second peak, and a jump discontinuity at twice the collision diameter) will remove these unusual characteristics, while presumably increasing the maximum density slightly. A byproduct of our investigation is a lower bound on the maximum density for random sphere packings in d dimensions, which is sharper than a well-known lower bound for regular lattice packings for $d \geq 3$.

1. Introduction

Over a broad range of length scales, many-particle systems exhibit a rich variety of structures with varying degrees of long-range order, spanning from crystals, quasicrystals, and polycrystals to amorphous solids and liquids. Consequently, it is natural to focus attention on the statistical mechanics of the arrangement of the particles. In the case of a macroscopic system containing a large number N of particles, a full configurational description of that system usually is neither feasible, desirable, nor necessary. For most practical purposes, it suffices to determine, or to describe, the distribution functions of low orders $n \ll N$. Conventionally, this information is conveyed in the form of correlation functions. For statistically homogeneous systems consisting of identical spherical particles in a volume V , these correlation functions are defined so that $\rho^n g^{(n)}(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_n)$ is proportional to the probability density for simultaneously finding n particles at locations $\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_n$ within the system,¹ where $\rho = N/V$ is the number density. With this convention, each $g^{(n)}$ approaches unity when all particle positions become widely separated within V .

The present study concerns the special circumstances for which the constituent particles are spherically symmetric and identical, and the system is statistically homogeneous and isotropic. These conditions can be satisfied if the system contains a single fluid or amorphous solid phase. The correlation function of primary interest is $g^{(2)}(r_{12})$, depending configurationally just on scalar pair distance r_{12} , and thus specifying how many pair

distances of a given length occur statistically within the system. The third-order function $g^{(3)}(r_{12}, r_{13}, r_{23})$ reveals how these pair separations are linked into triangles. This additional information strictly speaking cannot be inferred from the knowledge of $g \equiv g^{(2)}$ alone, although the Kirkwood superposition approximation^{1,2} presumes to fill that knowledge gap. The fourth-order function $g^{(4)}$ controls the assembly of triangles into tetrahedra, and is the lowest-order correlation function that is sensitive to *chirality* of the medium.

On account of their probability interpretation, all of the $g^{(n)}$ must be non-negative; in particular, for all $r \geq 0$ we must have

$$g(r) \geq 0 \quad (1)$$

In addition to this fundamental constraint, $g(r)$ is also subject to another basic inequality that arises from its connection to density fluctuations. This concerns the behavior of the structure factor defined thus³

$$\begin{aligned} S(k) &= 1 + \rho \int \exp(-i\mathbf{k}\cdot\mathbf{r}) [g(r) - 1] d\mathbf{r} \\ &= 1 + 4\pi\rho \int_0^{\infty} r \frac{\sin kr}{k} [g(r) - 1] dr \end{aligned} \quad (2)$$

The second line assumes that we are treating three-dimensional systems. The second fundamental constraint is the non-negativity of $S(k)$, i.e.,

$$S(k) \geq 0 \quad (3)$$

which must be obeyed for all real values of k . It should be noted that (1) and (3) are not at all restricted to states of thermal

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equilibrium but are more general. It is currently unknown if these necessary conditions (1) and (3) are also sufficient to guarantee that any function satisfying them is actually the pair correlation function for a realizable many-particle system; however, no counterexamples are currently known.

Two recent studies^{4,5} have examined the theoretical possibility of controlling pair interactions in an isothermal many-particle system over a nonvanishing density range, starting at $\rho = 0$, in such a way that $g(r)$ remains invariant over that range. The cases examined have assigned forms to the invariant g that were the zero-density limits appropriate for rigid rods, disks, and spheres,⁴ and for the hard core plus square well pair potential.⁵ In each of these examples an upper terminal density ρ^* could be identified such that over

$$0 \leq \rho \leq \rho^* \quad (4)$$

the g invariance could indeed be maintained. However, crossing ρ^* would cause the $S(k)$ inequality (3) to be violated at some k .

The principal objective of the present project is to apply the g -invariance technique to the still-challenging problem of random packings of spheres. It has now been well established that the old concepts of “random loose packing” and “random close packing” are ill-defined.⁷ Instead, a nontrivial density range exists over which irregular packings of various types (locally, collectively, or strictly jammed¹¹) can be formed, the preferred densities and local structures of which depend on the preparation algorithm. Our objective has been to study the logical connections between qualifying rigid-sphere g 's and the maximum corresponding densities, emerging as the terminal ρ^* 's.

Section 2 introduces a parametric family of qualitatively reasonable, but functionally elementary, pair correlation functions for the amorphous-state sphere spatial arrangement problem. This family contains a set of five adjustable parameters, whose values must of course be consistent with the two basic inequalities (1) and (3). Section 3 describes a numerical search procedure over these parameters, and its results, the goal of which was to produce the largest ρ^* . We believe it is significant that even with such a simple parametric family of pair correlation functions, ρ^* can come close to that obtained in many experimental and simulational preparations of random sphere packings. Section 4 offers some interpretive remarks stimulated by the numerical results in section 3 and indicates the natural and useful directions for future investigation. Finally, in an appendix, we derive a lower bound on the maximum density ρ^* for random sphere packings in d dimensions and show that it is sharper than a well-known lower bound for regular lattice packings for $d \geq 3$.

2. Model Family

Our interest in this paper is to study models in which long-range order is suppressed and short-range order is controlled. Information that is available from previous determinations of local order in amorphous sphere packings provides useful guidance in choosing a model family of functions for the present investigation. In particular, we note that a survey of several experimental and computer-simulation protocols,^{8–10} using distinct packing preparation procedures, appear to agree on the presence of some qualitative features. (Figure 1 shows the pair correlation function for a dense random packing of spheres as generated by us employing the Lubachevsky–Stillinger “compression” protocol.¹⁰) Using the sphere–pair distance of closest approach as the natural length unit, these $g(r)$ attributes are the following:

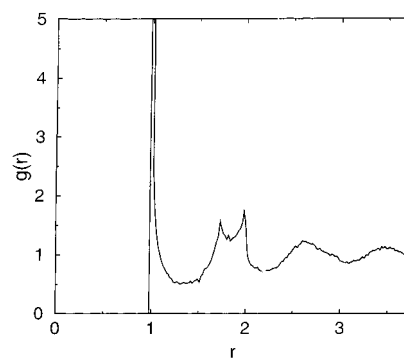


Figure 1. Pair correlation function $g(r)$ vs r as obtained by averaging over 10 configurations at a packing fraction $\phi = 0.64$. The “binned” peak value of $g(1)$ (not shown) is approximately 24.

- (i) Obviously, $g(r)$ must vanish for all $0 \leq r \leq 1$.
- (ii) On account of the jamming, virtually all spheres (a few “rattler” spheres can be present as exceptions) are rigidly in contact with neighbors. The number of such contacts must average at least 4 to meet the definition of “local” jamming.¹¹
- (iii) For $r \geq 1$, $g(r)$ displays finite-amplitude oscillations about unity, which decay to zero with increasing r . The length scale of these oscillations is roughly comparable to the sphere diameter.
- (iv) A pair of distinctive $g(r)$ peaks appear at distances approximately equal to $\sqrt{3}$ and $\sqrt{4}$. These are often termed a “split second peak”, and appear in modified form for amorphous deposits of soft-sphere and attracting particles.¹⁴
- (v) As r increases through $r = 2$, $g(r)$ experiences a discontinuous drop in magnitude.

It is not the objective of the present work to try to include all of these features slavishly. Instead, we have chosen as a first step to represent only attributes i–iii by a simple parametric function family, and to see how close the largest corresponding density would come to the approximate experimental range^{12,13} of “random” packing densities:¹⁵

$$1.18 \leq \rho \leq 1.26 \quad (5)$$

The equivalent approximate range of covering or packing fractions $\phi \equiv \pi\rho/6$ is

$$0.62 \leq \phi \leq 0.66 \quad (6)$$

Computer-simulation determinations of random packing fractions⁷ lie in the wider range

$$0.60 \leq \phi \leq 0.68 \quad (7)$$

illustrating the fact that the packing densities are protocol-dependent and hence non-unique.^{6,7} After the fact, this approach should determine how important the remaining attributes iv and v are for the random sphere packing problem.

Consequently, we have elected to write $g(r)$ as a linear combination of three portions, corresponding respectively to (i), (ii), and (iii) above:

$$g(r) = g_I(r) + g_{II}(r) + g_{III}(r) \quad (8)$$

The first involves just the unit step function U :

$$g_I(r) = U(r - 1) \quad (9)$$

while the second represents the sphere contacts:

$$g_{\text{II}}(r) = \frac{Z}{4\pi\rho} \delta(r-1) \quad (10)$$

Here, Z is the first of our adjustable parameters, equal to the mean number of contacts (coordination number) experienced by each sphere. The third portion contains four more adjustable dimensionless parameters (A, B, C, D):

$$g_{\text{III}}(r) = \frac{A}{r} \exp(-r/B) \sin\left(\frac{2\pi r}{C} + D\right) U(r-1) \quad (11)$$

and is intended to represent approximately the damped oscillation beyond contact.

The Fourier transforms required to evaluate the structure factor,

$$S(k) = 1 + \rho[G_{\text{I}}(k) + G_{\text{II}}(k) + G_{\text{III}}(k)] \quad (12)$$

are expressible entirely in terms of elementary functions:

$$\begin{aligned} G_{\text{I}}(k) &= \int \exp(-i\mathbf{k}\cdot\mathbf{r})[g_{\text{I}}(r) - 1] \, d\mathbf{r} \\ &= \frac{4\pi}{k^3} [k \cos k - \sin k] \end{aligned} \quad (13)$$

$$\begin{aligned} G_{\text{II}}(k) &= \int \exp(-i\mathbf{k}\cdot\mathbf{r})[g_{\text{II}}(r) - 1] \, d\mathbf{r} \\ &= \frac{Z \sin k}{\rho k} \end{aligned} \quad (14)$$

$$\begin{aligned} G_{\text{III}}(k) &= \int \exp(-i\mathbf{k}\cdot\mathbf{r})[g_{\text{III}}(r) - 1] \, d\mathbf{r} \\ &= \frac{2\pi \exp(-B)}{k} \\ &\left[\frac{B \cos(k-C-D) - (k-C) \sin(k-C-D)}{B^2 + (k-C)^2} - \frac{B \cos(k+C+D) - (k+C) \sin(k+C+D)}{B^2 + (k+C)^2} \right] \end{aligned} \quad (15)$$

The five adjustable parameters $Z, A, B, C,$ and D are subject to some obvious constraints. Clearly, we must demand that

$$Z \geq 0 \quad (16)$$

In addition, an exponential increase with r is not permissible, so

$$B \geq 0 \quad (17)$$

Furthermore, D only needs to span a single period of the trigonometrical factor in which it occurs:

$$0 \leq D \leq 2\pi \quad (18)$$

The remaining parameter pair A, C is not entirely free, of course, but must be consistent with both inequalities (1) and (3). Our central objective is to search over the five-dimensional domain defined by (1), (3), and (16)–(18), for the maximum terminal density $\rho^*(Z, A, B, C, D)$ or terminal covering volume fraction $\phi^*(Z, A, B, C, D)$ that they permit. Under the working assumption that this maximum is attained at the boundary of the five-

TABLE 1: Terminal Packing Fractions ϕ^* for Six Different Cases in Which the Step-Function Contribution g_{I} to g in (8) Is Always Included

case	$g_{\text{II}} \neq 0$	$g_{\text{III}} \neq 0$	$S(k) > 0$	ϕ^*
case I	$g_{\text{II}} \neq 0$	$g_{\text{III}} \neq 0$	$S(k) > 0$	$\phi^* = 0.627$
case II	$g_{\text{II}} \neq 0$	$g_{\text{III}} \neq 0$	$S(k) = 0$	$\phi^* = 0.46$
case III	$g_{\text{II}} \neq 0$	$g_{\text{III}} = 0$	$S(k) > 0$	$\phi^* = 0.41$
case IV	$g_{\text{II}} \neq 0$	$g_{\text{III}} = 0$	$S(k) = 0$	$\phi^* = 0.3125$
case V	$g_{\text{II}} = 0$	$g_{\text{III}} \neq 0$	$S(k) > 0$	$\phi^* = 0.375$
case VI	$g_{\text{II}} = 0$	$g_{\text{III}} \neq 0$	$S(k) = 0$	$\phi^* = 0.3535$

dimensional domain, it becomes important to know which constraint or constraints are at issue there, and why.

3. Numerical Search Procedure and Results

The problem of finding the maximal packing fraction $\phi^*(Z, A, B, C, D)$ can be posed as an optimization problem. Specifically, this can be posed as a two-level “min-max” problem: one wants to maximize $\phi(Z, A, B, C, D)$ over the parameters $Z, A, B, C,$ and D with the restrictions (16)–(18) such that the minimum of $S(k; Z, A, B, C, D)$ in the variable k and the minimum of $g(r; Z, A, B, C, D)$ in the variable r are both non-negative, i.e.,

$$\max_{Z, A, B, C, D} \phi \quad (19)$$

such that

$$\min_k S(k; Z, A, B, C, D) \geq 0 \quad \min_r g(r; Z, A, B, C, D) \geq 0 \quad (20)$$

The interval-arithmetic paradigm¹⁶ is a global optimization methodology that in principle should enable one to obtain exact narrow interval bounds on the maximal packing fraction in a computationally efficient manner. We attempted this calculation using the GlobSol Fortran 90 global optimization library¹⁷ but could not obtain an exact interval solution. This program is best suited for finding conventional extrema of simple differentiable functions with simple constraints. Our problem is considerably more complex and so we instead used GlobSol to find the minimum

$$\min_k S(k; Z, A, B, C, D)$$

and then employed a brute-force grid search over $Z, A, B, C,$ and D subject to the aforementioned conditions in order to maximize ϕ .

The search procedure is implemented for six different cases summarized in Table 1. In the first case (case I), no restrictions on the functions, other than the ones described above, are imposed. In the remaining cases, we impose additional restrictions. In particular, it is known that dense random packings are typically spatially uniform, implying that $S(k=0) \approx 0$. Therefore, in some instances, we carry out the search subject to the condition that $S(k=0) = 0$.

Case I. Not surprisingly, the least restrictive case yields the largest value of the maximal packing fraction: $\phi^* = 0.627$. The corresponding values of the parameters are listed in Table 2. Figure 2 shows the structure factor and pair correlation function. These functions reveal structural features that are not characteristic of typical dense random packings obtained either experimentally or computationally. For example, the structure factor at $k = 0$ is unusually high, implying significant density fluctuations in the infinite-wavelength limit. Moreover, at three different finite wavelengths ($k \approx 3.1, k \approx 6.3,$ and $k \approx 10$) the structure factor is essentially zero or nearly zero, implying

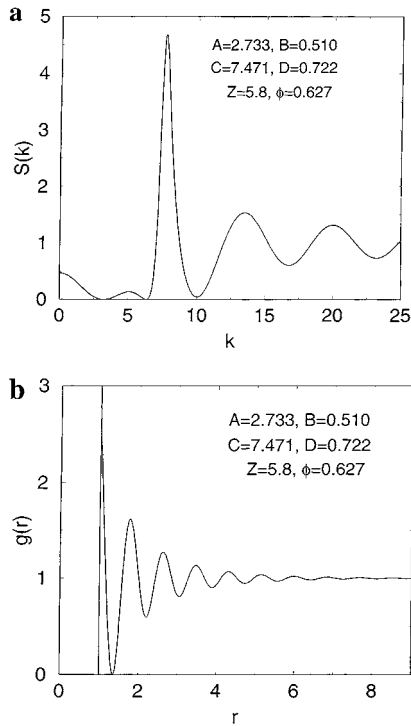


Figure 2. Structure factor (a) and pair correlation function (b) for case I. Note the appearance of a vertical line at contact in (b), indicating a δ -function contribution there.

TABLE 2: Values of the Parameters for the Cases in Table 1

case I	A = 2.733	B = 0.510	C = 7.471	D = 0.627	Z = 5.80
case II	A = 1.15	B = 0.510	C = 5.90	D = 1.66	Z = 2.3964
case III	A = 0	B = 0	C = 0	D = 0	Z = 3.1504
case IV	A = 0	B = 0	C = 0	D = 0	Z = 1.5
case V	A = 4.8	B = 1.2	C = 5.90	D = 0.90	Z = 0
case VI	A = 3.9	B = 0.9	C = 5.70	D = 0.90	Z = 0

vanishingly small density fluctuations at these wavelengths. Atypically, the pair correlation function $g(r)$ exhibits appreciable oscillations before attaining its long-range value at about $r = 8$. This feature could be the result of polycrystallinity, but the fact that $g(r)$ vanishes at $r \approx 1.4$ (another anomalous characteristic) evidently eliminates the possibility that such putative crystallites are face-centered cubic arrangements. Interestingly, the coordination number $Z \approx 5.8$ is approximately equal to the value observed in experiments and simulations of typical dense random packings.^{7–9} Theoretical arguments have been put forth predicting that $Z = 6$ for random packings of identical frictionless spheres in three dimensions.^{18–20}

Case II. In the second case, we conduct the search under the condition that $S(k=0) = 0$. For this condition to hold, Z must be given by

$$Z = 8\phi - 1 - \frac{24\phi}{B^2 + C^2} \left[\left(B + \frac{B^2 - C^2}{B^2 + C^2} \right) \sin(C + D) + \left(C + \frac{2BC}{B^2 + C^2} \right) \cos(C + D) \right] \quad (21)$$

This condition also implies that the term in $S(k)$ of order k^2 is zero, and therefore the first nonzero term is of order k^4 . Both the maximal packing fraction and coordination number drop from the first case to the values $\phi^* = 0.46$ and $Z = 2.3964$ (see Tables 1 and 2). Figure 3 shows the structure factor and pair correlation function. Note the atypical curvature of the function $g(r)$ near the contact value.

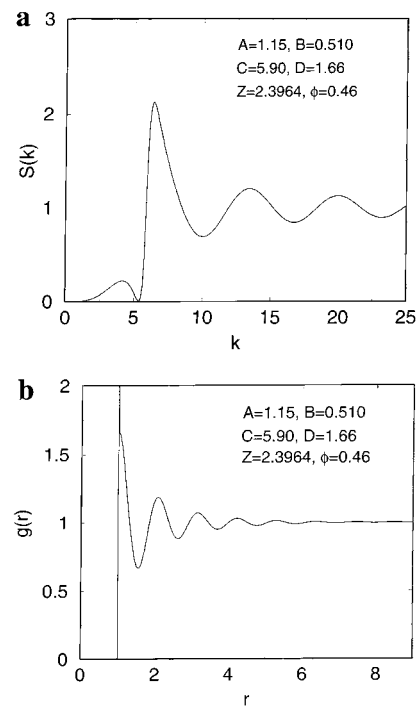


Figure 3. Structure factor (a) and pair correlation function (b) for case II. Note the appearance of a vertical line at contact in (b), indicating a δ -function contribution there.

Case III. In the third case, we suppress the damped-oscillating component [$g_{\text{III}}(r) = G_{\text{III}}(k) = 0$]. Here we find that $\phi^* = 0.41$ and $Z = 3.1504$.

Case IV. In the fourth case, we suppress the damped-oscillating component [$g_{\text{III}}(r) = G_{\text{III}}(k) = 0$] and we also impose the condition $S(k=0) = 0$. This problem can be solved exactly. Here we find

$$\phi^* = \frac{5}{16} \quad Z = \frac{3}{2} \quad (22)$$

In the Appendix, we obtain the d -dimensional generalization of this result and show how it leads to a lower bound on ϕ^* for the general case in which the third component is not suppressed [$g_{\text{III}}(r) \neq 0$, $G_{\text{III}}(k) \neq 0$].

Case V. In the fifth case, we suppress the δ -function component ($Z = 0$). Here we obtain $\phi^* = 0.375$ (see Tables 1 and 2).

Case VI. In the sixth case, we suppress the δ -function component ($Z = 0$) and we also impose the condition $S(k=0) = 0$. We find that $\phi^* = 0.3535$ (see Tables 1 and 2).

4. Concluding Remarks

For the family of pair correlation functions specified by (8), the optimal packing fraction is characterized by unusual structural features such as substantially large density fluctuations in the infinite-wavelength limit, vanishing or nearly vanishing fluctuations at several finite wavelength values, and an interparticle radial distance ($r \approx 1.4$) at which particle centers are prohibited. Nonetheless, the maximal packing fraction and coordination number ($\phi^* = 0.627$ and $Z = 5.8$) are consistent with values for dense random packings generated experimentally and computationally. Clearly, however, properties iv and v (“split second peak” and the discontinuous drop at $r = 2$) that are characteristic of typical random packings are absent in the optimal solution. In future work, one may want to consider other families of functions that are not as smooth as (8) away from

$r = 1$, e.g., piecewise continuous functions. Such extensions would quantify the significance of properties iv and v in raising ϕ^* above the optimal value of 0.627, while presumably driving $S(k=0)$ downward toward zero.

Assuming that the optimal packing can actually be realized, there remain many open questions. Do the spheres form a contacting percolating network? Given the high density that is achieved, we suspect that the answer is in the affirmative. If so, what is the geometry of the contact set? Are rattlers present in the optimal solution? Is the packing locally, collectively, or strictly jammed?¹¹ The answers to all of these questions would greatly be facilitated if we could determine whether there are packings that achieve the optimal solution. This can be accomplished using stochastic reconstruction techniques that enable one to obtain realizations of sphere packings that have a targeted pair correlation function or structure factor.²¹ We will attempt such a reconstruction in a future study. Another interesting extension of the present work is to generalize the family of pair correlation functions to the case of spheres of different sizes and to determine the maximal packing fraction.

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Appendix: d -Dimensional Generalization of Case IV

In this appendix, we obtain an exact expression for the optimal value of ϕ^* for the d -dimensional generalization of case IV. A consequence of this result is a lower bound on ϕ^* for random sphere packings in d dimensions, which we compare to a well-known lower bound for regular lattice packings.

Consider the evaluation of the structure factor $S(k)$ of relation 12 in d dimensions but without the short-ranged (damped-oscillating) contribution, i.e.,

$$S(k) = 1 + \rho[G_I(k) + G_{II}(k)] \quad (23)$$

where $G_I(k)$ and $G_{II}(k)$ are the d -dimensional Fourier transforms²²

$$G_I(k) = (2\pi)^{d/2} \int_0^\infty r^{d-1} \{g_I(r) - 1\} \frac{J_{(d/2)-1}(kr)}{(kr)^{(d/2)-1}} dr \quad (24)$$

$$G_{II}(k) = (2\pi)^{d/2} \int_0^\infty r^{d-1} \{g_{II}(r) - 1\} \frac{J_{(d/2)-1}(kr)}{(kr)^{(d/2)-1}} dr \quad (25)$$

$$g_I(r) = U(r - 1) \quad (26)$$

$$g_{II}(r) = \frac{Z}{s_1(1)\rho} \delta(r - 1) \quad (27)$$

and

$$s_1(r) = \frac{2\pi^{d/2} r^{d-1}}{\Gamma(d/2)} \quad (28)$$

The quantity $s_1(r)$ is the surface area of a d -dimensional sphere of radius r .

It immediately follows that

$$\rho G_I(k) = - \frac{2^{3d/2} \Gamma(1 + d/2) \phi}{(k)^{d/2}} J_{d/2}(k) \quad (29)$$

where

$$\phi = \rho \frac{\pi^{d/2}}{\Gamma(1 + d/2)} (1/2)^d \quad (30)$$

is the d -dimensional packing fraction. If this were the only contribution to the structure factor, then the non-negativity condition $S(k) \geq 0$ implies

$$\phi^* = \frac{1}{2^d} \quad (31)$$

which agrees with the result given in ref 4. It easily follows that

$$\rho G_{II}(k) = \frac{2^{d/2} \Gamma(1 + d/2) Z}{d(k)^{d/2-1}} J_{d/2-1}(k) \quad (32)$$

Substitution of (29) and (32) into (23) yields

$$S(k) = 1 + (Z - 2^d \phi) + \left[\frac{2^{d-2} \phi}{1 + d/2} - \frac{Z}{2d} \right] k^2 + \mathcal{O}(k^4) \quad (33)$$

The last explicit term changes sign if Z increases past $2^d \phi d / (d + 2)$. At this crossover point,

$$S(k) = 1 - \frac{2^{d+1}}{d + 2} \phi + \mathcal{O}(k^4) \quad (34)$$

Since the minimum occurs at $k = 0$, then we have the exact results

$$\phi^* = \frac{d + 2}{2^{d+1}} \quad Z = \frac{d}{2} \quad (35)$$

Thus, we have the lower bound

$$\phi^* \geq \frac{d + 2}{2^{d+1}} \quad (36)$$

for random sphere packings in d dimensions because the addition of the short-range contribution (which we have neglected) would result in a generally larger value of ϕ^* . In obtaining the lower bound (36), we have assumed there are no further sufficiency conditions beyond (1) and (3).

In very high dimensions ($d \sim 1000$), the densest known packings are *nonregular* lattices.²³ Thus, it is of interest to compare the lower bound (36) to the Minkowski–Hlawka theorem,²³ which gives a lower bound on the maximum packing fraction for d -dimensional *regular* lattices of identical spheres:

$$\phi_{\max} \geq \frac{\zeta(d)}{2^{d-1}} \quad (37)$$

where $\zeta(d)$ is the Riemann ζ function. The lower bound (36) is larger than the lower bound (37) for $d \geq 3$. Indeed, the difference between these bounds grows with increasing d .

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