

Mean Nearest-Neighbor Distance in Random Packings of Hard D -Dimensional Spheres

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We derive the first nontrivial rigorous bounds on the mean distance between nearest neighbors λ in ergodic, isotropic packings of hard D -dimensional spheres that depend on the packing fraction and nearest-neighbor distribution function. Several interesting implications of these bounds for equilibrium as well as nonequilibrium ensembles are explored. For an equilibrium ensemble, we find accurate analytical approximations for λ for $D = 2$ and 3 that apply up to random close packing. Our theoretical results are in excellent agreement with available computer-simulation data.

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Random packings of hard spheres and disks have been used to model a wide variety of physical systems, including liquids [1,2], glasses [3], colloidal dispersions [4], porous media [5], composite materials [6], powders [7], cell membranes [8], and thin films [9]. In contrast to *ordered sphere packings* in D dimensions [10], few rigorous results concerning the structure of random packings of hard D -dimensional spheres have been established. For example, the *mean distance between nearest neighbors* λ in random sphere packings, a basic and experimentally accessible measure of the structure, is not well understood theoretically for $D \geq 2$. Knowledge of λ is of importance in diverse fields that span between the physical sciences (e.g., controlling the structure of ceramics [11]) and the biological sciences (e.g., characterizing spatial patterns in animal and plant populations [12] and in organisms [13]).

In this Letter, we derive the first rigorous bounds on λ for ergodic ensembles of statistically isotropic packings of identical D -dimensional hard spheres [14] that depend on the sphere packing fraction ϕ and the contact value of a certain pair distribution function G (defined below). These results are stated in the form of three theorems and corollaries which immediately follow from them. Several interesting implications of these bounds for equilibrium as well as nonequilibrium ensembles are explored. In the special case of an equilibrium ensemble, we also find accurate analytical approximations for λ for hard spheres ($D = 3$) and disks ($D = 2$) that apply for the full density range, i.e., up to random close packing.

Consider general ergodic ensembles of statistically isotropic packings of hard D -dimensional spheres of *unit diameter* at number density ρ . The *mean distance between nearest neighbors* λ is given by [15]

$$\lambda = 1 + \int_1^\infty \exp[-2^D D \phi \int_1^r G(y) y^{D-1} dy] dr, \quad (1)$$

where $G(r)$ is the *nearest-neighbor conditional pair distribution function*. The quantity $\rho s(r)G(r) dr$ is the probability that particle centers lie in a spherical shell of radius r and volume $s(r) dr$, given that there are no other particle centers in this spherical region except for a particle located at the origin. Here $s(r)$ is the surface area of a D -

dimensional sphere of radius r and ϕ is the *sphere packing fraction*. Clearly, $G(r) = 0$ for $r < 1$. $G(r)$ should not be confused with the *radial distribution function* $g(r)$ which does not exclude other sphere centers besides the one at the origin. Clearly, the contact values are the same, i.e., $G(1) = g(1)$. $G(r)$ and hence λ cannot be obtained exactly for $D \geq 2$ [15].

Theorem 1: For any ergodic ensemble of isotropic packings of identical, D -dimensional hard spheres in which $G(1) \leq G(r)$ for $1 \leq r \leq \infty$,

$$\lambda \leq 1 + 1/D 2^D \phi G(1). \quad (2)$$

Proof: Since $G(1) \leq G(r)$ for $1 \leq r \leq \infty$, then (1) leads to the upper bound

$$\lambda \leq 1 + \int_1^\infty \exp[-2^D \phi G(1)(r^D - 1)] dr. \quad (3)$$

The integral of (3) can be further simplified by transforming to the variable $u = r - 1$, giving

$$\lambda \leq 1 + \int_0^\infty \exp[-2^D \phi G(1) \times (u^D + Du^{D-1} + \dots + Du)] du. \quad (4)$$

Since each term of the polynomial $u^D + Du^{D-1} + \dots + Du$ is positive, the integral of (4) is bounded from above by retaining only the *linear term* Du , yielding bound (2).

Corollary 1.1: In the special case of an equilibrium ensemble of isotropic packings of identical, D -dimensional hard spheres, the mean distance λ is related to the thermodynamic pressure p , absolute temperature T , and Boltzmann's constant k by the inequality

$$\lambda \leq 1 + 1/2D(p/\rho kT - 1). \quad (5)$$

This follows from Theorem 1, the fact that the reduced equation of state $p/\rho kT = 1 + 2^{D-1} \phi G(1)$ [1,2], and that for equilibrium ensembles (*the most random distribution of spheres subject to the impenetrability constraint*) $G(r)$ is a *monotonically increasing function of r* [1,15]. This ensemble is a useful model of a wide class of systems outside the context of liquids, e.g., suspensions, packed beds, powders, etc. The constraint (5) could be

used to make new rigorous statements about the phase diagram of hard-sphere systems.

We now apply Theorem 1 to another important ergodic ensemble, namely, the nonequilibrium *random sequential addition* (RSA) process, produced by randomly, irreversibly, and sequentially placing nonoverlapping objects into a volume [16–19]. The adsorption of proteins on solid surfaces [17] and certain coagulation processes [18] are well modeled by the RSA process, for example. For identical D -dimensional RSA spheres, the filling process terminates at the *jamming limit* at which λ must be greater than unity. Clearly, this jamming limit will be less than the *random-close-packing limit* [20] for equilibrium hard spheres where λ is exactly unity. However, since the radial distribution function at contact $g(1)$ [or equivalently $G(1)$] diverges as ϕ approaches the jamming limit [17], Theorem 1 leads to the contradictory result that $\lambda = 1$ at the jamming limit. Since RSA spheres are ergodic and isotropic, it follows that $G(r)$ near the jamming limit is not always less than the contact value $G(1)$ for $1 \leq r \leq \infty$. On physical grounds, it is clear that for sufficiently large r , $G(r)$ must be larger than $G(1)$. In summary, $G(r)$ is a *nonmonotonic* function of r for any D for RSA spheres in contrast to equilibrium spheres. This has been borne out by simulations, a subject of a future paper.

Theorem 2: For any ergodic ensemble of isotropic packings of identical, D -dimensional hard spheres in which $(1 - \phi)^{-1} \leq G(r)$ for $1 \leq r \leq \infty$,

$$\lambda \leq 1 + (1 - \phi)/D2^D \phi. \quad (6)$$

Proof: The proof of this theorem proceeds in the same fashion as for Theorem 1.

The condition $(1 - \phi)^{-1} \leq G(r)$ is true for a large class of ergodic ensembles, including the equilibrium ensemble [15]. We note that for equilibrium hard rods ($D = 1$), the upper bound (6) is exact since $G(r) = (1 - \phi)^{-1}$ and hence $\lambda = 1 + (1 - \phi)/2\phi$ [15].

To illustrate the utility of Theorem 2, we again examine the RSA process. For RSA rods ($D = 1$) at $\phi = 0.5$, Monte Carlo simulations have yielded $\lambda = 1.53$. Theorem 2, however, states that $\lambda \leq 1.5$ at $\phi = 0.5$. We conclude that $G(r)$ for RSA rods at $\phi = 0.5$ is not always larger than $(1 - \phi)^{-1} = 2$, in contrast to equilibrium rods. This conclusion is true for $\phi > 0.5$ as well. Note that as $\phi \rightarrow 0$, RSA and equilibrium ensembles become identical [16].

Theorem 3: For any ergodic ensemble of isotropic packings of identical, D -dimensional hard spheres,

$$\lambda \leq 1 + 1/D2^D \phi. \quad (7)$$

Proof: For any ergodic, isotropic hard-sphere ensemble, it is always true that $G(r) \geq 1$ for $1 \leq r \leq \infty$, since $G(r) = 1$ applies to “point” particles, i.e., spatially uncorrelated spheres. Using this fact, the proof proceeds in the same fashion as for Theorem 1.

Theorem 1 is an ensemble-dependent result in that the mean distance λ is given in terms of the contact value $G(1)$.

By contrast, although the inequalities of Theorems 2 and 3 are weaker than (2), they are also more general in that they depend only on the packing fraction ϕ . Theorem 3, the most general bound, has some interesting corollaries which we now state.

Corollary 3.1: Any packing of identical, D -dimensional hard spheres in which the mean distance obeys the relation

$$\lambda > 1 + 1/D2^D \phi \quad (8)$$

cannot be ergodic and isotropic.

Relation (8) defines a region in the ϕ - λ plane which is prohibited to ergodic, isotropic packings, and thus Corollary 3.1 provides a quantitative and experimentally measurable criterion to ascertain when a hard-sphere system is *definitely not ergodic and isotropic*. Examples of *non-ergodic, anisotropic ensembles* that obey (8) are periodic cubic arrays at sufficiently small packing fractions. For example, for periodic hard rods ($D = 1$), $\lambda = 1 + (1 - \phi)/\phi$, and hence this system satisfies (8) for all $\phi < 1/2$. Figures 1 and 2 depict the region prohibited to ergodic, isotropic systems for $D = 3$ and $D = 2$, respectively.

Corollary 3.2: As the dimension D of any ergodic ensemble of isotropic packings of identical, hard spheres increases, the mean distance drops off at least as fast as $(D2^D)^{-1}$ and approaches unity for nonzero ϕ in the limit $D \rightarrow \infty$. The maximum packing fraction ϕ_c in turn approaches zero in the limit $D \rightarrow \infty$.

To our knowledge, this is the first rigorous proof that $\phi_c \rightarrow 0$ as $D \rightarrow \infty$ for ergodic hard-sphere systems. Figure 3 shows how the upper bound on λ of Theorem 3 dramatically drops off as D is increased. Corollary 3.2

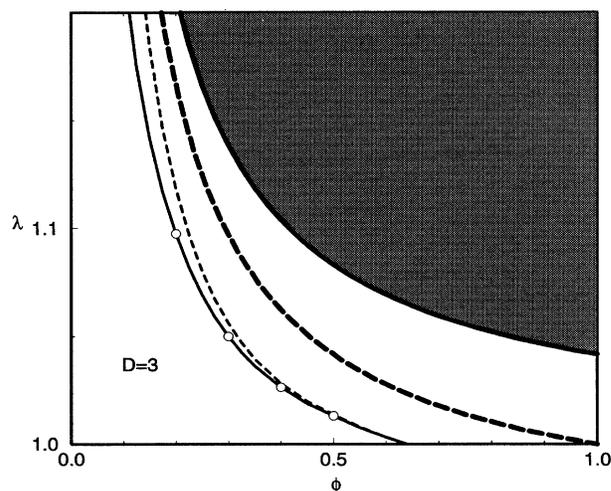


FIG. 1. Mean nearest-neighbor distance λ (in units of diameter) vs packing fraction ϕ for hard spheres ($D = 3$). This solid line is equilibrium prediction from (1) and (10). Open circles are corresponding simulation data [25]. Thin dashed line is upper bound of Theorem 1 for an equilibrium ensemble from (17). Thick dashed and solid lines are upper bounds of Theorems 2 and 3, respectively. Shaded region is prohibited to ergodic, isotropic hard spheres according to Corollary 3.1.

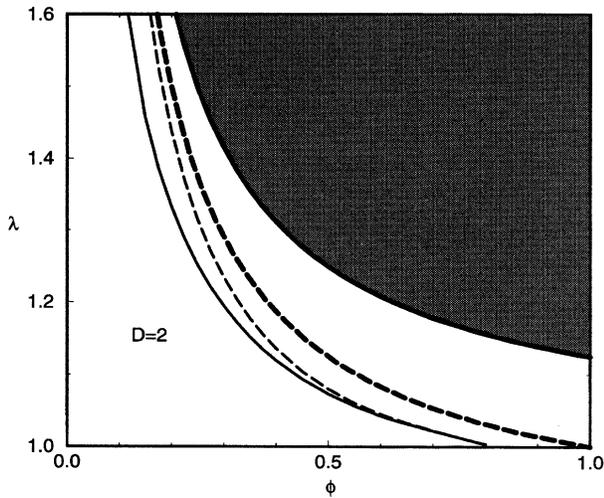


FIG. 2. Mean nearest-neighbor distance λ (in units of diameter) vs packing fraction ϕ for hard disks ($D = 2$). Thin solid line is equilibrium prediction from (1) and (14). Thin dashed line is upper bound of Theorem 1 for an equilibrium ensemble from (18). Thick dashed and solid lines are upper bounds of Theorems 2 and 3, respectively. Shaded region is prohibited to ergodic, isotropic hard disks according to Corollary 3.1.

implies the interesting fact that all ensembles (equilibrium or not) lose their distinction as D is made large. The fact that the maximum packing fraction ϕ_c decreases with increasing D is consistent with random-close-packing experiments for $D = 2$ ($\phi_c \approx 0.82$ [21]) and $D = 3$ ($\phi_c \approx 0.64$ [21]). For hard rods ($D = 1$), ϕ_c is trivially unity. For RSA ensembles, $\phi_c \approx 0.75$ for $D = 1$ [16], $\phi_c \approx 0.55$ for $D = 2$ [17], and $\phi_c \approx 0.38$ for $D = 3$ [18], where ϕ_c is the jamming limit.

We now obtain the mean distance λ by deriving new expressions for the distribution function $G(r)$ for an equilibrium ensemble of hard spheres that are accurate for all densities, including the metastable branch from the

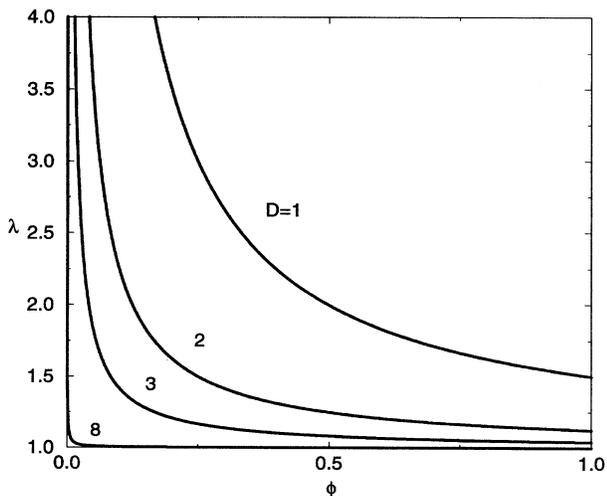


FIG. 3. Upper bound on λ of Theorem 3 vs packing fraction ϕ for several D .

freezing point ϕ_f up to the random-close-packing fraction ϕ_c [22]. For $D = 2$ and 3, Torquato, Lu, and Rubinstein [15] derived approximations for $G(r)$ that were shown to be accurate up to the freezing density. Their procedure relies on knowing accurately the contact value of the radial distribution function $g(1)$ or, equivalently, $G(1)$. They explored several traditional choices for $G(1)$ that possess poles at $\phi = 1$. Such classical expressions are in good agreement with simulation data up to the freezing packing fraction ϕ_f but diverge from the data for ϕ larger than ϕ_f [2]. Indeed, they predict a close-packing fraction at the unphysical value $\phi = 1$ and hence are inadequate for ϕ near ϕ_c . We therefore seek relations for $g(1)$ or $G(1)$ that are accurate up to ϕ_c .

Song, Stratt, and Mason [2] have argued that $g(1)$ diverges for ϕ near ϕ_c according to the scaling law

$$g(1) = G(1) \sim (\phi_c - \phi)^{-s}, \quad \phi \rightarrow \phi_c. \quad (9)$$

Recent simulations [23] suggest that $s = 1$ for $D = 2$ and 3 ($s = 1$ exactly for $D = 1$).

We make use of an important observation, namely, that the functional nature of $g(1)$ between dilute and freezing densities is fundamentally different than that between freezing and random close packing. A simple form for $g(1)$ is assumed between freezing and random close packing that incorporates the correct pole at ϕ_c [cf. (9)], enabling us to find both accurate and simple expressions for $G(r)$ and, hence, the mean distance λ . Simulation data [2] reveals that, to an excellent approximation, $g^{-1}(1)$ decreases linearly from its value of $g_f^{-1}(1)$ at $\phi = \phi_f$ to zero at the random-close-packing fraction $\phi = \phi_c$. Thus, for $\phi_f \leq \phi \leq \phi_c$, we assume that $G(1) = g_f(1)(\phi_c - \phi_f)/(\phi_c - \phi)$. For $0 \leq \phi \leq \phi_f$, we will employ expressions possessing poles at $\phi = 1$ as described below. Our expressions for $g^{-1}(1)$ are in very good agreement with the empirical fits of Song, Stratt, and Mason [2] for all ϕ , i.e., $0 \leq \phi \leq \phi_c$.

We can use this information on $g(1)$, in a similar manner [20] to that employed by Torquato, Lu, and Rubinstein [15], to obtain the following relations for $G(r)$ for both $D = 3$ and 2. Specifically, for equilibrium hard spheres ($D = 3$), we find

$$G(r) = a_0 + a_1/r + a_2/r^2, \quad r \geq 1, \quad (10)$$

where the coefficients a_0 , a_1 , and a_2 are given by

$$a_0 = \begin{cases} \frac{1 + \phi + \phi^2 - \phi^3}{(1 - \phi)^3}, & 0 \leq \phi \leq \phi_f, \\ 1 + 4\phi g_f(1) \frac{\phi_c - \phi_f}{\phi_c - \phi}, & \phi_f \leq \phi \leq \phi_c, \end{cases} \quad (11)$$

$$a_1 = \begin{cases} \frac{\phi(3\phi^2 - 4\phi - 3)}{2(1 - \phi)^3}, & 0 \leq \phi \leq \phi_f, \\ \frac{3\phi - 4}{2(1 - \phi)} + 2(1 - 3\phi)g_f(1) \frac{\phi_c - \phi_f}{\phi_c - \phi}, & \phi_f \leq \phi \leq \phi_c, \end{cases} \quad (12)$$

$$a_2 = \begin{cases} \frac{\phi^2(2 - \phi)}{2(1 - \phi)}, & 0 \leq \phi \leq \phi_f, \\ \frac{2 - \phi}{2(1 - \phi)} + (2\phi - 1)g_f(1) \frac{\phi_c - \phi_f}{\phi_c - \phi}, & \phi_f \leq \phi \leq \phi_c. \end{cases} \quad (13)$$

Here $\phi_f = 0.49$ [24], $\phi_c = 0.64$ [21], and $g_f(1) = (1 - \phi_f/2)/(1 - \phi_f)^3$.

In the case of equilibrium hard disks ($D = 2$), we find

$$G(r) = a_0 + a_1/r, \quad r \geq 1, \quad (14)$$

where the coefficients a_0 and a_1 are given by

$$a_0 = \begin{cases} \frac{1+0.128\phi}{(1-\phi)^2}, & 0 \leq \phi \leq \phi_f, \\ 2g_f(1)\frac{\phi_c-\phi_f}{\phi_c-\phi} - \frac{1}{1-\phi}, & \phi_f \leq \phi \leq \phi_c, \end{cases} \quad (15)$$

$$a_1 = \begin{cases} \frac{-0.564\phi}{(1-\phi)^2}, & 0 \leq \phi \leq \phi_f, \\ -g_f(1)\frac{\phi_c-\phi_f}{\phi_c-\phi} + \frac{1}{1-\phi}, & \phi_f \leq \phi \leq \phi_c. \end{cases} \quad (16)$$

Here $\phi_f = 0.69$ [24], $\phi_c = 0.82$ [21], and $g_f(1) = (1 - 0.436\phi_f)/(1 - \phi_f)^2$.

Note that when $r = 1$, both expressions (10) and (14) ϕ in the vicinity of ϕ_c are consistent with the asymptotic relation (10) with a critical exponent $s = 1$.

In the special case of an equilibrium ensemble of particles, bound (2) of Theorem 1 can be written explicitly for $D = 3$ and 2 using the aforementioned approximations for $G(1)$. For $D = 3$, using (2) and (10), we find

$$\lambda \leq \begin{cases} 1 + \frac{(1-\phi)^3}{24\phi(1-\phi/2)}, & 0 \leq \phi \leq \phi_f, \\ 1 + \frac{\phi_c-\phi}{24\phi g_f(1)(\phi_c-\phi_f)}, & \phi_f \leq \phi \leq \phi_c. \end{cases} \quad (17)$$

For $D = 2$, using (2) and (14), we have

$$\lambda \leq \begin{cases} 1 + \frac{(1-\phi)^2}{8\phi(1-0.436\phi)}, & 0 \leq \phi \leq \phi_f, \\ 1 + \frac{\phi_c-\phi}{8\phi g_f(1)(\phi_c-\phi_f)}, & \phi_f \leq \phi \leq \phi_c. \end{cases} \quad (18)$$

Figure 1 depicts our prediction (thin solid line) of the mean nearest-neighbor distance λ for equilibrium hard spheres ($D = 3$) versus the packing fraction ϕ . Our prediction is seen to be in excellent agreement with available simulation data (open circles) [25]. In the limit $\phi \rightarrow \phi_c = 0.64$, our prediction of λ correctly goes to unity, in contrast with the prediction of Ref. [15] in which λ does not go to unity until $\phi \rightarrow 1$. Included in the figure are the bounds of Theorems 1, 2, and 3. The upper bound of Theorem 1 is very sharp for packing fractions between freezing and random close packing, becoming exact in the limit $\phi \rightarrow \phi_c$.

In Fig. 2 we show our prediction of the mean distance λ for hard disks ($D = 2$) versus the packing fraction ϕ . Our prediction of λ again correctly goes to unity in the limit that $\phi \rightarrow \phi_c = 0.82$. The figure includes the upper bounds of Theorems 1, 2, and 3.

Finally, we note that the methods and results described here can be extended to treat hard spheres with a polydispersivity in size.

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