Nearest-neighbor statistics for packings of hard spheres and disks

S. Torquato,*

Princeton Materials Institute and Department of Civil Engineering and Operations Research, Princeton University, Princeton, New Jersey 08540

The probability of finding a nearest neighbor at some radial distance from a given particle in a system of interacting particles is of fundamental importance in a host of fields in the physical as well as biological sciences. A procedure is developed to obtain analytical expressions for nearest-neighbor probability functions for random isotropic packings of hard D-dimensional spheres that are accurate for all densities, i.e., up to the random close-packing fraction. Using these results, the mean nearest-neighbor distance λ as a function of the packing fraction is computed for such many-body systems and compared to rigorous bounds on λ derived here. Our theoretical results are found to be in excellent agreement with available computer-simulation data.

I. INTRODUCTION

Systems of many interacting particles are ubiquitous in nature and in man-made situations. In considering such many-body systems, a very natural question to ask is, What is the effect of the nearest neighbor on some reference particle in the system? The answer to this question requires knowledge of the nearest-neighbor distribution function $H(r)$, i.e., the probability density associated with finding a nearest neighbor at some radial distance r from the reference particle. From $H(r)$ one can determine other quantities of fundamental interest such as the *mean nearest-neighbor distance between particles* and, in the case of sphere packings, *the random close-packing density*. Knowledge of $H(r)$ and λ is of fundamental importance in a host of fields in the physical and biological sciences, including the molecular nature of liquids and amorphous solids [1–11], transport processes in heterogeneous materials [12,13], stellar dynamics [14], spatial patterns in biological systems [15], and the processing of ceramics [16].

Hertz [17] evaluated $H(r)$ for a three-dimensional system of "point" particles, i.e., particles whose centers are randomly (Poisson) distributed. The D-dimensional generalization of Hertz's solution for Poisson distributed points at number density ρ is given by [18]

$$H(r) = \rho \frac{dv(r)}{dr} \exp[-\rho v(r)] \quad , \tag{1}$$

where $v(r)$ is the volume of a D-dimensional sphere of radius r [cf. Eq. (16)]. In general, relation (1) is a poor approximation to the nearest-neighbor distribution function of systems of finite-size interacting particles.

A major influence on the structure of a many-body system of finite-size particles is that brought about by their mutual volume exclusion, particularly at high densities irrespective of attractive interparticle forces that may be present [19]. For this reason, random packings of hard spheres and disks have been used to model a wide variety of materials such as liquids [19], glasses [20], suspensions [11], porous media [21], particulate composites [22], fiber-reinforced materials [23], powders [24], cell membranes [25], and thin films [26], to mention but a few examples. This paper focuses on obtaining analytical expressions for $H(r)$ of random isotropic packings of D-dimensional hard spheres for the entire density range, i.e., up to the random close packing density.

Torquato, Lu, and Rubinstein (TLR) [18,27] derived an exact analytical series representation of $H(r)$ for isotropic distributions of identical interacting D-dimensional spheres at number density ρ in terms of multidimensional integrals over the so-called n-particle probability density functions $\rho_1, \rho_2, \ldots, \rho_n$. The quantity $\rho_n(\mathbf{r}_1, \ldots, \mathbf{r}_n)$ characterizes the probability of finding a configuration of n spheres with centers at positions $\mathbf{r}_1, \ldots, \mathbf{r}_n$, respectively. For spatially uncorrelated or Poisson distributed centers, ρ_n is trivially a constant equal to ρ^n and the TLR series expression leads to the simple formula (1).

For an *equilibrium ensemble* of hard rods ($D = 1$), the ρ_n for any n are known exactly, permitting an exact evaluation of $H(r)$ (see the Appendix). For $D \geq 2$, however, such exact and complete knowledge of the ρ_n for any n is not possible for equilibrium ensembles of hard spheres, implying that an exact solution of $H(r)$ for $D \geq 2$ for general (equilibrium and nonequilibrium) ensembles is out of the question. In the case of equilibrium ensembles of hard disks ($D = 2$) and hard spheres ($D = 3$), therefore, TLR derived relations for $H(r)$ that amounted to summing the TLR series approximately. Their nearest-neighbor expressions were shown to be accurate over a wide range of densities, namely, up to the freezing point [28]. TLR noted, however, that their expressions must necessarily break down near random close packing because they possess poles at the unphysical packing volume fraction of unity.

*Electronic address: torquato@matter.princeton.edu

One of the main aims of the present paper is to formulate expressions for the nearest-neighbor distribution function $H(r)$ for equilibrium ensembles of isotropic packings of hard spheres ($D = 3$) and of hard disks ($D = 2$) of diameter σ that are accurate for all densities, including the metastable branch from freezing up to random close packing. Our procedure is based on knowing the contact value of the radial distribution function $g(\sigma)$. We make use of an important observation, namely, that the functional nature of $g(\sigma)$ between dilute and freezing densities is fundamentally different from that between freezing and random close packing. A simple form for $g(\sigma)$ is assumed between freezing and random close packing that incorporates a pole at the random close-packing density, enabling us to find simultaneously accurate and simple expressions for $H(r)$ and hence the mean nearest-neighbor distance λ.

In Sec. II, we define and discuss the nearest-neighbor distribution function and closely related auxiliary functions for systems of identical, interacting D-dimensional spheres in general and statistically homogeneous and isotropic packings of hard spheres in particular. In Sec. III, we derive expressions for the nearest-neighbor functions for an equilibrium ensemble of isotropic packings of hard spheres ($D = 3$) that are accurate for all particle packing fractions, i.e., up to random close packing. In Sec. IV, we carry out analogous calculations for hard disks ($D = 2$). In Sec. V, we apply our results to compute the mean nearest-neighbor distance λ for equilibrium, D-dimensional hard spheres as a function of the particle packing fraction. Here we also derive rigorous bounds on λ and compare them to our predictions. Finally, we make concluding remarks in Sec. VI.

II. DEFINITIONS AND GENERAL RELATIONS

A. Nearest-neighbor functions

We consider nearest-neighbor functions for statistically homogeneous and isotropic systems of identical, D-

dimensional spheres of diameter σ at a number density ρ. The potential of interaction is arbitrary within the class of physically meaningful microstructures. We define the nearest-neighbor distribution function $H(r)$ (for $0 \le r \le +\infty$) as follows:

$H(r)dr = $ probability that the center of the nearest
particle from any reference particle
(centered at the origin) is at a distance
between r and $r + dr$.   (2)

Note that $H(r)$ is a probability density function (having dimensions of inverse length) and normalizes to unity, i.e.,

$$\int_0^\infty H(r)dr = 1 .   (3)$$

It is useful to express the nearest-neighbor distribution function as a product of two related nearest-neighbor functions as follows:

$$H(r) = \rho s(r) G(r) E(r) ,   (4)$$

where the *exclusion probability function* $E(r)$ is defined by

$E(r) = $ probability that, given that a reference particle
is centered at the origin, a spherical region
of radius r encompassing this reference particle
is empty of particle centers   (5)

and the *conditional pair distribution function* $G(r)$ is defined by

$\rho s(r) G(r) dr = $ probability that particle centers lie in a spherical shell of radius r and volume $s(r)dr$
(centered at the origin), given that there are no other particle centers in this spherical region,
except for a particle located at the origin.   (6)

Here $s(r)$ is the surface area of a D-dimensional sphere of radius r,

$$s(r) = \frac{2\pi^{D/2} r^{D-1}}{\Gamma(D/2)} .   (7)$$

For example, for $D = 1, 2,$ and 3, $s(r) = 2, 2\pi r,$ and $4\pi r^2$, respectively.

It follows that $E(r)$ in (5) is the *cumulative distribution function* associated with the probability density $H(r)$ and hence

$$E(r) = 1 - \int_0^r H(y)dy .   (8)$$

The integral above represents the probability of finding at least one particle center in the spherical region around the respective reference particle. Differentiating (8) yields

$$H(r) = \frac{-\partial E(r)}{\partial r} .   (9)$$

From the relations given above, it is simple to show that the exclusion probability $E(r)$ is related to the conditional pair distribution function $G(r)$ via the expression

$$E(r) = \exp\left[-\int_0^r \rho s(y) G(y) dy \right] .   (10)$$

The combination of (4) and (10) yields

$$H(r) = \rho s(r) G(r) \exp\left[-\int_0^r \rho s(y) G(y) dy\right] \ . \quad (11)$$

In summary, one can compute the function $H(r)$ given either the exclusion probability function $E(r)$ [cf. (9)] or the pair distribution function $G(r)$ [cf. (11)].

TLR [18] found rigorous successive upper and lower bounds on the nearest-neighbor functions. One of the simplest inequalities worth noting here is the following lower bound:

$$G(r) \geq g(r) \ , \quad (12)$$

where $g(r)$ is the well-known radial distribution function which characterizes the probability of finding *any* particle (not necessarily the nearest particle) a radial distance r away from a particle at the origin. Observe that when $r = \sigma$, $G(\sigma)$ is precisely equal to $g(\sigma)$, the radial distribution function at contact.

B. Hard-sphere systems

Consider now statistically homogeneous and isotropic ensembles of mutually impenetrable (hard) spheres of diameter σ, i.e., systems of spheres characterized by a pair potential which is zero when the interparticle distance r is greater than σ and infinite when $r \leq \sigma$. Calculations of the nearest-neighbor distribution function $H(r)$ and the auxiliary quantities, the exclusion probability $E(r)$ and conditional pair distribution function $G(r)$, are generally nontrivial for such models for $D \geq 2$. For $D = 1$, an exact solution is possible (see the Appendix). In the hard-core region, the following exact relations always apply:

$$E(r) = 1, \quad H(r) = G(r) = 0 \quad \text{for } 0 \leq r \leq \sigma. \quad (13)$$

Reiss, Frisch, and Lebowitz [1] have studied functions closely related to the nearest-neighbor functions that TLR [18] have referred to as *void* nearest-neighbor functions [27]. For example, $G_V(r)$ is the "void" conditional pair distribution function in which the reference point is any arbitrary point in the system rather than the center of a sphere as in the case of $G(r)$. TLR have shown that

$$G_V(r) = G(r), \qquad r \geq \sigma \ . \quad (14)$$

However, for the range $0 \leq r \leq \sigma$, $G_V(r) \neq G(r)$ [18]. Strictly speaking, Eq. (14) applies to *ergodic* ensembles [29] of isotropic D-dimensional hard spheres *in equilibrium*. An equilibrium ensemble of statistically homogeneous and isotropic D-dimensional hard spheres, roughly speaking, is the most random distribution of spheres subject to the condition of impenetrability.

Reiss *et al.* [1] determined a number of exact conditions that the function $G_V(r)$ must satisfy for ergodic ensembles of isotropic hard spheres. For example, $G_V(r)$ and its first spatial derivative must be continuous at $r = \sigma/2$. We note that

$$G_V(r) = \frac{1}{1 - \rho v(r)} \qquad \text{for } 0 \leq r \leq \sigma/2, \quad (15)$$

where $v(r)$ is the volume of a D-dimensional sphere of radius r,

$$v(r) = \frac{\pi^{D/2} r^D}{\Gamma(1 + D/2)} \ . \quad (16)$$

For example, for $D = 1$, 2, and 3, $v(r) = 2r$, πr^2, and $4\pi r^3/3$, respectively. Moreover, for an equilibrium ensemble of D-dimensional hard spheres one can relate $G_V(r)$ at contact ($r = \sigma$) to this function at $r = \infty$ for $D=1$, 2, and 3, respectively, according to

$$a_0 \equiv G_V(\infty) = G_V(\sigma), \quad (17)$$
$$a_0 \equiv G_V(\infty) = 1 + 2\phi G_V(\sigma), \quad (18)$$
$$a_0 \equiv G_V(\infty) = 1 + 4\phi G_V(\sigma). \quad (19)$$

Here a_0 is the reduced equation of state, i.e.,

$$a_0 = \frac{p}{\rho k T}, \quad (20)$$

where p is the pressure, T is absolute temperature, k is Boltzmann's constant, and

$$\phi = \rho v(\sigma/2) \quad (21)$$

is the D-dimensional *particle packing fraction*. Finally, we note that for an equilibrium hard-sphere ensemble, $G(r)$ is a monotonically increasing function of r [1].

C. Mean nearest-neighbor distances and random close packing

Consider a general ensemble of statistically homogeneous and isotropic of D-dimensional spheres of diameter σ with arbitrary interparticle interaction. A very useful and convenient measure of the structure of such systems is the *mean nearest-neighbor distance between particles* λ, which is defined as the first moment of $H(r)$, i.e.,

$$\lambda = \int_0^\infty r H(r) dr \ . \quad (22)$$

In the special case of ergodic ensembles of isotropic hard spheres of diameter σ, the mean nearest-neighbor distance between particles λ is given as

$$\lambda = \int_\sigma^\infty r H(r) dr \ , \quad (23)$$

which is equivalent to

$$\lambda = \sigma + \int_\sigma^\infty E(r) dr \ . \quad (24)$$

Since $E \geq 0$, then $\lambda \geq \sigma$.

Equation (23) or (24) can be used to operationally define the *random close-packing fraction* ϕ_c [18]. Specifically, one can define it to be the *maximum* packing frac-

tion over all *ergodic, isotropic ensembles [29] at which* $\lambda = \sigma$. This definition eliminates the possibility of a *random loose packing* of spheres for which $\lambda = \sigma$ but which is known to occur at a volume fraction lower than the random close-packing value [6]. It also eliminates (in the thermodynamic limit), the existence of trapped but un-jammed "rattler" spheres. When $\phi = \phi_c$, the functions $E(r)$ and $H(r)$ must obey the relations

$$E(r) = H(r) = 0 \qquad \text{for } r > \sigma. \tag{25}$$

We shall adopt the view that ϕ_c is equivalent to the packing fraction at which randomly arranged hard spheres cannot further be compressed by applying hydro-static pressure. According to this definition, the internal pressure must diverge to infinity as one approaches ϕ_c from below along the metastable branch. Song, Stratt, and Mason [8] have argued that this singularity (reflect-ing the limit of metastability of the hard-sphere fluid) is a special type of critical point. Specifically, they proposed that the pressure, or equivalently the radial distribution function at contact $g(\sigma)$, has the following asymptotic form in the vicinity of the critical point ϕ_c:

$$g(\sigma) = G(\sigma) \sim (\phi_c - \phi)^{-s} \qquad \text{for } \phi \to \phi_c. \tag{26}$$

Based upon simulation data, they determined that $s = 0.76$ for $D = 3$ and $s = 0.84$ for $D = 2$ (s is exactly unity for $D = 1$). More recent simulations [30] suggest that $s = 1$ in both two and three dimensions.

III. NEAREST-NEIGHBOR EXPRESSIONS FOR HARD SPHERES

In this section we will derive nearest-neighbor expres-sions for an equilibrium ensemble of statistically homoge-neous and isotropic hard spheres ($D = 3$). The case $D=3$ has probably the widest application as it can be used to model a variety of materials, including liquids [1–10,19], amorphous solids [4,5,20], suspensions [11], porous media [12,13], particulate composites [22], and powders [24].

TLR [18] obtained analytical expressions for the nearest-neighbor functions $H(x)$, $E(x)$, and $G(x)$ for equilibrium ensembles of D-dimensional hard-sphere sys-tems. Here we have introduced the dimensionless dis-tance

$$x \equiv \frac{r}{\sigma}. \tag{27}$$

Their procedure is based on knowing the contact value of the radial distribution function $g(1)$ or, equivalently, $G(1)$. They explored several choices for $G(1)$, includ-ing the scaled-particle and Carnahan-Starling approxi-mations. The scaled-particle relation is in good agree-ment with machine calculations, but is not as accurate as the Carnahan-Starling relation, especially near the freez-ing packing fraction ϕ_f (see Table I). However, both the Carnahan-Starling and scaled-particle relations possess poles at $\phi = 1$ and hence predict a close-packing frac-tion at the unphysical value $\phi = 1$. Therefore, such tra-ditional expressions for $g(1)$ are wholly inadequate for densities near random close packing. For this reason,

TABLE I. Some important packing fractions for D-dimensional hard-sphere systems. The freezing and ran-dom close-packing fractions are taken from Refs. [30] and [6], respectively.

State	Freezing packing fraction ϕ_f	Random close-packing fraction ϕ_c	Closest packing fraction
$D = 1$	1.0	1.0	1.0
$D = 2$	0.69	0.82	$\pi/(2\sqrt{3}) \approx 0.907$
$D = 3$	0.49	0.64	$\pi/(3\sqrt{2}) \approx 0.740$

TLR noted that while their nearest-neighbor expressions are accurate over a wide range of densities, these re-lations must necessarily break down near the random close-packing fraction ϕ_c. For example, we know that when $\phi = \phi_c$, the functions $E(x)$ and $H(x)$, according to relations (25), must be zero for all $x > 1$. The nearest-neighbor expressions of Ref. [18] do not obey relations (25) when $\phi = \phi_c$ however.

One of the main aims of this paper is to obtain an-alytical expressions for $H(x)$, $E(x)$, and $G(x)$ that are simultaneously simple and accurate up to the random close-packing fraction. This shall be accomplished by utilizing accurate expressions for the contact value of the radial distribution function $g(1)$ (which captures the salient features of random close packing [cf. (26)] and the related void conditional pair distribution function $G_V(x)$ described in Sec. II. We employ the void quan-tity $G_V(x)$ described only to the extent that it enables us to find approximations for $G(x)$ [via Eq. (14)] and, hence, $H(x)$ and $E(x)$. Relation (14) is an approxima-tion at very large ϕ since $G_V(x)$ cannot be equal to $G(x)$ when $\phi = \phi_c$. The study and determination of the void nearest-neighbor quantities between freezing and close-packing densities will be examined in detail in a future paper.

A. General determination of $G_V(x)$

Reiss and co-workers [1,2] have demonstrated that, for large x, the conditional void pair distribution function G_V has the following asymptotic form in arbitrary di-mension D:

$$G_V(x) = a_0 + \frac{a_1}{x} + \frac{a_2}{x^2} + \cdots + \frac{a_{D-1}}{x^{D-1}}. \tag{28}$$

They also showed that such a form is a good approxima-tion for small x and thus (28) is a good approximation for the entire range between $x = 1/2$ and $x = \infty$. Note that in the limit $x \to \infty$, $G_V(\infty)$ correctly equals the reduced equation of state a_0. For $D = 3$, Reiss *et al.* de-termined the coefficients a_0, a_1, and a_2 by utilizing three of the exact conditions mentioned in Sec. II, namely, the "infinity" condition (19) and the continuity of G_V and its first derivative at $x = 1/2$, given relation (15).

In order to obtain an accurate determination of the coefficients in the expression

$$G_V(x) = a_0 + \frac{a_1}{x} + \frac{a_2}{x^2} \qquad \text{for } x \geq 1/2 \tag{29}$$

at high densities for $D = 3$, we shall replace the condition on the first derivative of G_V at $x = 1/2$ with a condition on the contact value $G_V(1)$ (equal to the contact value of the radial distribution function). Thus the challenge before us is to utilize an expression for $G_V(1)$ that is accurate up to the random close-packing density.

To summarize, we will require an accurate expression for the contact value $G_V(1)$ up to random close packing and in addition will employ the conditions

$$a_0 \equiv G_V(\infty) = 1 + 4\phi G_V(1) \quad , \tag{30}$$

$$G_V(x = 1/2) = \frac{1}{1 - \phi} \quad . \tag{31}$$

These conditions yield the following equations for the three unknowns a_0, a_1, and a_2:

$$a_0 + a_1 + a_2 = G_V(1), \tag{32}$$

$$(4\phi - 1)a_0 + 4\phi a_1 + 4\phi a_2 = -1, \tag{33}$$

$$a_0 + 2a_1 + 4a_2 = \frac{1}{1 - \phi}. \tag{34}$$

Solving this system of equations yields that the coefficients of (29) are explicitly given in terms of $G_V(1)$ as follows:

$$a_0 = 1 + 4\phi G_V(1), \tag{35}$$

$$a_1 = \frac{3\phi - 4}{2(1 - \phi)} + 2(1 - 3\phi)G_V(1), \tag{36}$$

$$a_2 = \frac{2 - \phi}{2(1 - \phi)} + (2\phi - 1)G_V(1). \tag{37}$$

B. Accurate expressions for $g(1)$ up to random close packing

The determination of $G(x)$ for arbitrary values of x rests on having an accurate expression for the contact value of the radial distribution function $g(1)$ or, equivalently, $G(1)$, up to random close-packing densities. Song et al. [8] obtained empirical expressions for $g(1)$ for equilibrium ensembles up to random close packing by fitting the expression

$$g(1) = \sum_{n=1}^{D^2} \frac{c_n \phi^n}{(1 - \phi/\phi_c)^s} \quad , \qquad c_1 = 1 \tag{38}$$

to available computer simulation data for the entire packing fraction range, i.e., $0 \leq \phi \leq \phi_c$. As noted earlier, for $D = 3$ and $D = 2$ they found $s = 0.76$ and $s = 0.84$, respectively. They determined the coefficients c_n by matching the virial (density) expansion of $g(1)$ up to the order

indicated and found very good agreement with the data. Note that for $D = 3$, eight coefficients must be determined.

An examination of the figures in the paper by Song et al. reveals that traditional expressions for $g(1)$ that possess poles at $\phi = 1$, such as Carnahan-Starling and scaled-particle relations, are accurate up to the freezing packing fraction ϕ_f but increasingly diverge from the simulation data for ϕ larger than ϕ_f. Indeed, such expressions predict a close-packing fraction at the unphysical value of $\phi = 1$. This indicates that the nature and functional form of $g(1)$ must be different in the density range between freezing and random close packing. Moreover, it is important to note that the plot of the inverse contact value $g^{-1}(1)$ versus ϕ in the study of Song et al. reveals that $g^{-1}(1)$ decreases almost linearly from freezing to random close packing.

This motivates us to use the Carnahan-Starling expression

$$G(1) = \frac{(1 - \phi/2)}{(1 - \phi)^3} \qquad \text{for } 0 \leq \phi \leq \phi_f \tag{39}$$

and the relation

$$G(1) = g_f(1) \frac{(\phi_c - \phi_f)}{(\phi_c - \phi)} \qquad \text{for } \phi_f \leq \phi \leq \phi_c. \tag{40}$$

Here $g_f(1) = (1 - \phi_f/2)/(1 - \phi_f)^3$ denotes the contact value of the radial distribution function at the freezing packing fraction $\phi_f \approx 0.49$. The random close-packing fraction ϕ_c is taken to be 0.64 (see Table I). Equation (40) is obtained by assuming that $g^{-1}(1)$ decreases linearly from its value of $g_f^{-1}(1)$ at $\phi = \phi_f$ to zero at the random close-packing fraction $\phi = \phi_c$. Note that expression (40) is consistent with the asymptotic relation (26) with a critical exponent $s = 1$. This value of unity is slightly larger than the value used by Song et al., but is in agreement with more recent simulations [30].

In Fig. 1 we compare Eqs. (39) and (40) to the empirical fit of Song et al. It is seen that the simple relations (39) and (40) are in very good agreement with the empirical fit. More sophisticated approximations for $G(1)$ could have been used. We choose to employ relations (39) and (40) since they are simultaneously simple and accurate [33].

C. Accurate nearest-neighbor expressions up to freezing

We now apply the results of Secs. III A and III B to find accurate expressions for nearest-neighbor quantities in the packing fraction range $0 \leq \phi \leq \phi_f$. Use of the Carnahan-Starling relation (39) and Eq. (14) in conjunction with relations (29) and (35)–(37) yields the nearest-neighbor functions to be given by

$$G(x) = a_0 + \frac{a_1}{x} + \frac{a_2}{x^2} \qquad \text{for } x \geq 1, \tag{41}$$

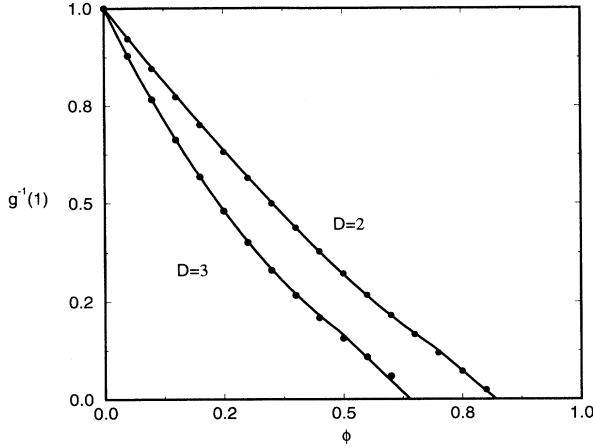$$E(x) = \exp\{-\phi[8a_0(x^3 - 1) \\ + 12a_1(x^2 - 1) + 24a_2(x - 1)]\} \quad \text{for } x \geq 1, \tag{42}$$

FIG. 1. Inverse of radial distribution function at contact $g^{-1}(1)$ vs packing fraction ϕ for hard spheres ($D = 3$) and hard disks ($D = 2$) of unit diameter. The solid curve for $D = 3$ is generated using relations (39) and (40). The solid curve for $D = 2$ is generated using relations (59) and (60). Filled circles are obtained from the empirical fit of Song et al. [8].

$$H(x) = 24\phi(a_0 x^2 + a_1 x + a_2)E(x) \qquad \text{for } x \geq 1. \quad (43)$$

The coefficients a_0, a_1, and a_2 are given by

$$a_0 = \frac{1 + \phi + \phi^2 - \phi^3}{(1 - \phi)^3}, \qquad (44)$$

$$a_1 = \frac{\phi(3\phi^2 - 4\phi - 3)}{2(1 - \phi)^3}, \qquad (45)$$

$$a_2 = \frac{\phi^2(2 - \phi)}{2(1 - \phi)^3}. \qquad (46)$$

Note that the left-hand side of (43) actually reads $\sigma H(x)$, but since we implicitly set $\sigma = 1$, we simply write $H(x)$ here and henceforth.

The relation for $G(x)$ given by TLR [18] uses the Carnahan-Starling relation (3.13), but does not satisfy the infinity condition (3.4). Thus the present relations (41)–(43) are to be employed over the corresponding relations in Ref. [18], even though they are numerically only slightly more accurate.

D. Accurate nearest-neighbor expressions from freezing to random close packing

Here we obtain nearest-neighbor expressions for densities between the freezing and the random close packing, the most difficult regime to treat theoretically. The combination of the new relation (40), Eq. (14) (an approximation for such large ϕ), and the expressions (35)–(37) gives

$$G(x) = a_0 + \frac{a_1}{x} + \frac{a_2}{x^2} \qquad \text{for } x \geq 1, \quad (47)$$

$$E(x) = \exp\{-\phi[8a_0(x^3 - 1) + 12a_1(x^2 - 1) \\ + 24a_2(x - 1)]\} \qquad \text{for } x \geq 1, \quad (48)$$

$$H(x) = 24\phi(a_0 x^2 + a_1 x + a_2)E(x) \qquad \text{for } x \geq 1. \quad (49)$$

The coefficients a_0, a_1, and a_2 are given by

$$a_0 = 1 + 4\phi g_f(1)\frac{(\phi_c - \phi_f)}{(\phi_c - \phi)}, \qquad (50)$$

$$a_1 = \frac{3\phi - 4}{2(1 - \phi)} + 2(1 - 3\phi)g_f(1)\frac{(\phi_c - \phi_f)}{(\phi_c - \phi)}, \qquad (51)$$

$$a_2 = \frac{2 - \phi}{2(1 - \phi)} + (2\phi - 1)g_f(1)\frac{(\phi_c - \phi_f)}{(\phi_c - \phi)}. \qquad (52)$$

It is important to emphasize that the relations (47)–(49) capture the salient feautures in the vicinity of random close packing. In particular, due to the existence of a pole at $\phi = \phi_c$, both $E(x)$ and $H(x)$ are zero for all $x > 1$ when $\phi = \phi_c$, i.e., the relations (48) and (49) obey (25). This is to be contrasted with the corresponding relations of Ref. [18] which do not obey conditions (25) because they do not incorporate information about the random close-packing state. This point is elaborated on below.

E. Discussion

Figure 2 depicts the exclusion probability $E(x)$ for a packing fraction below the freezing fraction ($\phi = 0.2$) and slightly above the freezing fraction ($\phi = 0.5$). The figure also compares our theory to available Monte Carlo simulation data [32]. Agreement between theory and the
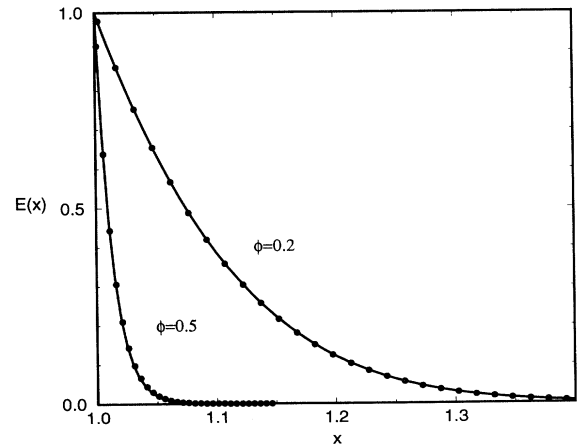

FIG. 2. Exclusion probability $E(x)$ for hard spheres ($D = 3$) of diameter σ vs dimensionless distance $x = r/\sigma$ at two different values of the packing fraction ϕ. Solid curves for $\phi = 0.2$ and $\phi = 0.5$ are obtained from Eqs. (42) and (48), respectively. Filled circles are corresponding simulation data [32].
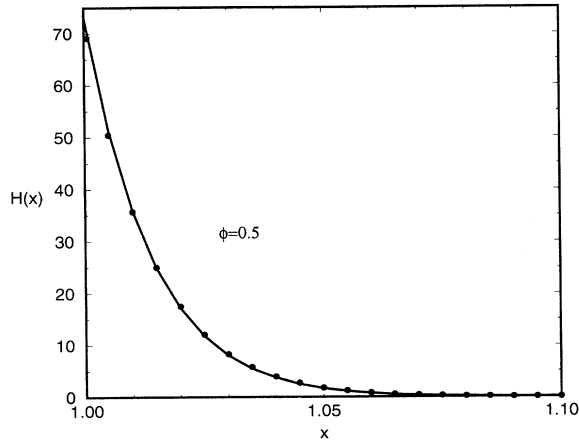
FIG. 3. Nearest-neighbor distribution function $H(x)$ for hard spheres ($D = 3$) of diameter σ vs dimensionless distance $x = r/\sigma$ at two different values of the packing fraction ϕ. Solid curves for $\phi = 0.2$ and $\phi = 0.5$ are obtained from Eqs. (43) and (49), respectively. Filled circles are corresponding simulation data [32].

simulation data is seen to be excellent. Figure 3 shows that our theoretical expression for the nearest-neighbor probability density function $H(x)$ is again in excellent agreement with simulation data for $\phi = 0.5$.

Figure 4 illustrates our results for the conditional pair distribution function $G(x)$ for several values of the packing fraction. As expected, $G(x)$ is a monotonically increasing function of x for fixed ϕ; it increases with increasing ϕ for fixed x.

Recall that the nearest-neighbor relations derived by TLR [18] are accurate up to freezing densities and thus agree well with the simulation data at $\phi = 0.5$, a value slightly higher than the freezing value $\phi_f = 0.49$. However, the TLR relations must break down near $\phi = \phi_c =$

0.64 because the only pole they possess is at the unphysical value $\phi = 1$. This implies that the TLR relations generally overstimate $E(x)$ and $H(x)$ near ϕ_c. Figure 5 compares our results for the exclusion probability $E(x)$ at a packing fraction value very near the random close packing ($\phi = 0.63$) to the corresponding TLR result. The TLR expression overestimates $E(x)$, especially for x near unity. The effective range of the TLR expression for $E(x)$ is about 6 times greater than that of relation (48) at this packing fraction. The mean nearest-neighbor distance λ predicted from the TLR relation turns out be almost twice as great at that obtained from relation (48).

How different are the nearest-neighbor functions for hard-sphere systems versus Hertz's Poisson (randomly overlapping) sphere systems [cf. Eq. (49)]? The answer was given by TLR [18], but it is worth repeating here. Exclusion-volume effects associated with hard cores lead to a nearest-neighbor distribution function $H(x)$, which is strikingly different from the corresponding quantity for spatially uncorrelated particles at nondilute conditions. For $x < 1$, unlike hard particles, $H(r) \neq 0$ for penetrable particles since their centers can come arbitrarily close to one another. For large x, $H(x)$ for penetrable particles is larger than $H(x)$ for hard particles since in the former system one is more likely to find larger void regions surrounding the central particle as the result of interparticle overlap. The behavior of $H(x)$ for these models for any D is qualitatively the same.

Finally, we mention that one can use our results for hard spheres of diameter σ to obtain nearest-neighbor functions for interpenetrating spheres in the *penetrable-concentric shell (cherry-pit)* model [34]. In this model each D-dimensional sphere of diameter σ is composed of a hard core of diameter $\epsilon\sigma$, encompassed by a perfectly penetrable concentric shell of thickness $(1 - \epsilon)\sigma/2$. The extreme limits of the impenetrability parameter $\epsilon = 0$ and $\epsilon = 1$ correspond to the cases of fully penetrable and totally impenetrable spheres, respectively. Given our totally-impenetrable-sphere results of Secs. III and IV,
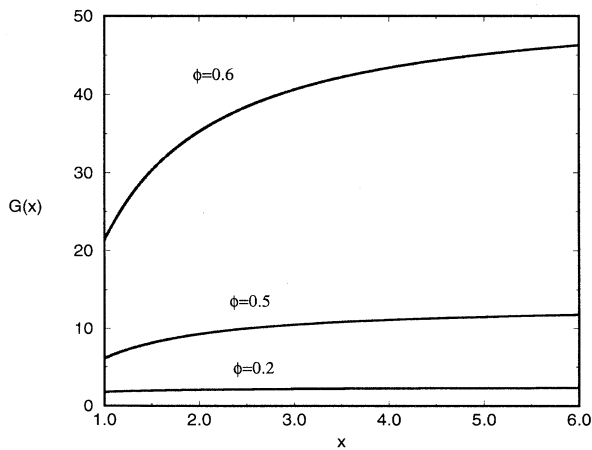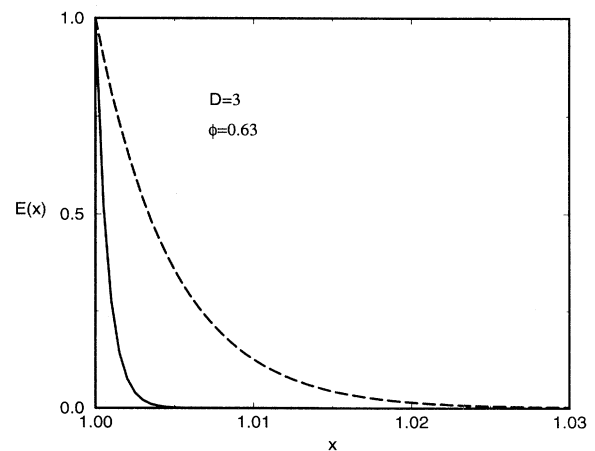

FIG. 4. Conditional pair distribution function $G(x)$ for hard spheres ($D = 3$) of diameter σ vs dimensionless distance $x = r/\sigma$ at three different values of the packing fraction ϕ. The curve for $\phi = 0.2$ is obtained from Eq. (41) and curves for $\phi = 0.5$ and $\phi = 0.6$ are obtained from Eq. (47).

FIG. 5. Comparison of exclusion probability $E(x)$ for hard spheres ($D = 3$) of diameter σ vs dimensionless distance $x = r/\sigma$ obtained from Eq. (42) (solid curve) and Eq. (5.22) (dashed curve) of Ref. [18] for $\phi = 0.63$.

one can obtain the corresponding results for penetrable spheres ($\epsilon < 1$) by simply replacing σ (on the right-hand sides of the relations) with $\epsilon\sigma$. For example, in the fully penetrable case ($\epsilon = 0$), this procedure allows one to recover Hertz's solution (1).

IV. NEAREST-NEIGHBOR EXPRESSIONS FOR HARD DISKS

The procedure described above for $D = 3$ is followed here to obtain analogous nearest-neighbor relations for an equilibrium ensemble of isotropic hard disks ($D = 2$). Our main aim again is to improve upon the predictive capability of existing relations [18] in the vicinity of the random close-packing fraction ϕ_c. Hard-disk systems are reasonable models of fiber-reinforced materials [22], certain types of cell membranes [25], and thin films [26].

A. General determination of $G_V(x)$

For $D = 2$, we assume that the conditional void pair distribution function is of the form

$$G_V(x) = a_0 + \frac{a_1}{x} \qquad \text{for } x \geq 1/2. \tag{53}$$

In order to determine the coefficients a_0 and a_1 we will require an accurate expression for the contact value of the radial distribution function as well as the condition

$$G_V(x = 1/2) = \frac{1}{1 - \phi} . \tag{54}$$

These conditions yield the following system of equations:

$$a_0 + a_1 = G_V(1), \tag{55}$$

$$a_0 + 2a_1 = \frac{1}{1 - \phi}. \tag{56}$$

Solving this system of equations yields that the coefficients of (53) are explicitly given in terms of $G_V(1)$ as

$$a_0 = 2G_V(1) - \frac{1}{1 - \phi}, \tag{57}$$

$$a_1 = -G_V(1) + \frac{1}{1 - \phi}. \tag{58}$$

B. Accurate expressions for $g(1)$ up to random close packing

Here we follow the same procedure that we used for $D = 3$, i.e., for densities below freezing we employ an expression that possesses a pole at $\phi = 1$ and for densities between freezing and random close packing we assume that $g^{-1}(1)$ decreases linearly from its freezing value. Specifically, we employ the expression

$$G(1) = \frac{(1 - 0.436\phi)}{(1 - \phi)^2} \qquad \text{for } 0 \leq \phi \leq \phi_f \tag{59}$$

and the relation

$$G(1) = g_f(1)\frac{(\phi_c - \phi_f)}{(\phi_c - \phi)} \qquad \text{for } \phi_f \leq \phi \leq \phi_c. \tag{60}$$

Here $g_f(1) = (1 - 0.436\phi)/(1 - \phi_f)^2$ is the contact value of the radial distribution function at the freezing packing fraction $\phi_f \approx 0.69$. The random close-packing fraction ϕ_c is taken to be 0.82 (see Table I).

Equation (59) is obtained by assuming the form

$$G(1) = \frac{(1 + c\phi)}{(1 - \phi)^2} \tag{61}$$

and determining the coefficient c by requiring that this form give the correct third virial coefficient. We note that the scaled-particle expression for $D = 2$

$$G(1) = \frac{(1 - \phi/2)}{(1 - \phi)^2} \tag{62}$$

was used in the TLR study. Relation (59) is somewhat more accurate than the scaled-particle relation at densities near freezing.

Figure 1 shows that the agreement between the relations (59) and (60) and the corresponding empirical fit of Song et al. [8] is very good.

C. Accurate nearest-neighbor expressions up to freezing

Here we use the results of the previous two subsections to obtain accurate expressions for nearest-neighbor quantities in the range $0 \leq \phi \leq \phi_f$. Use of relation (59) and Eq. (14) in conjunction with the general relations (57) and (58) yields

$$G(x) = a_0 + \frac{a_1}{x} \qquad \text{for } x \geq 1, \tag{63}$$

$$E(x) = \exp[-\phi(4a_0(x^2 - 1) + 8a_1(x - 1)] \qquad \text{for } x \geq 1, \tag{64}$$

$$H(x) = 8\phi(a_0 x + a_1)E(x) \qquad \text{for } x \geq 1. \tag{65}$$

The coefficients are a_0 and a_1 are given by

$$a_0 = \frac{1 + 0.128\phi}{(1 - \phi)^2}, \tag{66}$$

$$a_1 = \frac{-0.564\phi}{(1 - \phi)^2}. \tag{67}$$

Relations (63)–(65) are slightly more accurate than the corresponding TLR expressions because the present relations use the more accurate expression (59) for $G(1)$.

D. Accurate nearest-neighbor expressions from freezing to random close packing

We now obtain nearest-neighbor relations for densities between freezing and random close packing. The combination of the relation (60), Eq. (14) (an aproximation in this density range), and general relations (57) and (58) yields

$$G(x) = a_0 + \frac{a_1}{x} \qquad \text{for } x \geq 1, \tag{68}$$

$$E(x) = \exp\{-\phi[4a_0(x^2 - 1) + 8a_1(x - 1)]\} \quad \text{for } x \geq 1 , \tag{69}$$

$$H(x) = 8\phi(a_0 x + a_1)E(x) \qquad \text{for } x \geq 1. \tag{70}$$

The coefficients a_0 and a_1 are given by

$$a_0 = 2g_f(1)\frac{(\phi_c - \phi_f)}{(\phi_c - \phi)} - \frac{1}{1 - \phi}, \tag{71}$$

$$a_1 = -g_f(1)\frac{(\phi_c - \phi_f)}{(\phi_c - \phi)} + \frac{1}{1 - \phi}. \tag{72}$$

Relations (68)–(70) are clearly superior to the corresponding TLR relations near ϕ_c for reasons already noted.

E. Discussion

Figure 6 shows the nearest-neighbor probability density function $H(x)$ for $D = 1, 2$, and 3 at $\phi = 0.3$. Since the packing efficiency increases as D increases, $H(x)$ for x near unity increases with increasing D. In Fig. 7 we compare the expression (69) for $E(x)$ to the correspond-
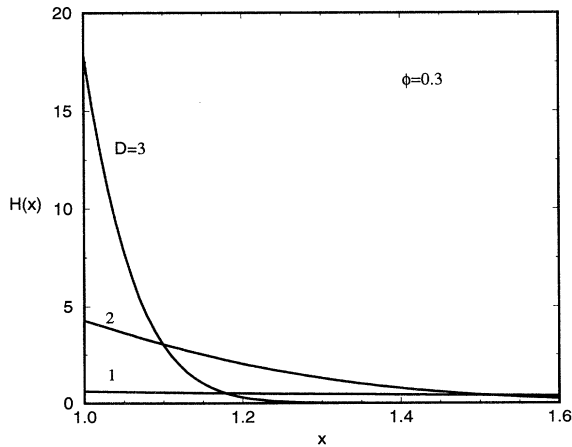

FIG. 6. Nearest-neighbor distribution function $H(x)$ for D-dimensional hard spheres of diameter σ vs dimensionless distance $x = r/\sigma$ for $D = 1$, 2, and 3 at a packing fraction $\phi = 0.3$. Curves for $D = 3$, $D = 2$, and $D = 1$ are obtained from Eqs. (49), (70), and (A2), respectively.

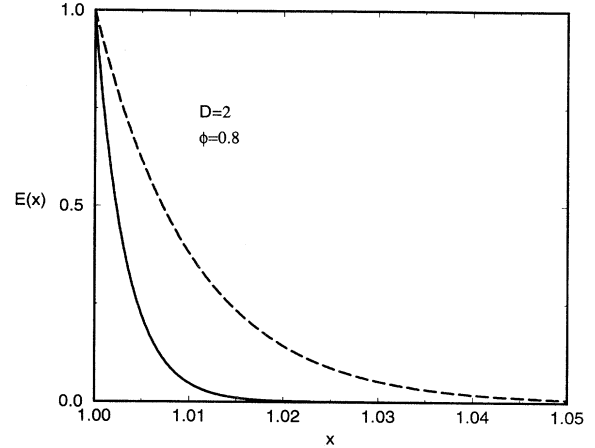

FIG. 7. Comparison of exclusion probability $E(x)$ for hard disks ($D = 2$) of diameter σ vs dimensionless distance $x = r/\sigma$ obtained from Eq. (48) (solid curve) and Eq. (5.13) (dashed curve) of Ref. [18] for $\phi = 0.8$

ing TLR relation for $\phi = 0.8$, a packing fraction value very near random close packing $\phi_c = 0.82$. We again see that the TLR relation generally overestimates $E(x)$, especially for x near unity.

V. MEAN NEAREST-NEIGHBOR DISTANCE BETWEEN D-DIMENSIONAL HARD SPHERES

The mean nearest-neighbor distance between particles λ is defined by either (23) or (24). In dimensionless terms, (24) can be written as

$$\frac{\lambda}{\sigma} = 1 + \int_1^\infty E(x)dx$$

$$= 1 + \int_1^\infty \exp\left[-2^D D\phi \int_1^x G(y)y^{D-1}dy\right]. \tag{73}$$

In arriving at (73) we have used (7), (10), and (21) and that $G(x) = 0$ for $0 \leq x < 1$. Relation (73) is valid for any ergodic, isotropic ensemble of D-dimensional hard spheres.

Before evaluating (73) for the mean nearest-neighbor distance λ/σ of equilibrium hard-sphere ensembles using the nearest-neighbor relations developed in the previous sections, we first derive rigorous relations and bounds on λ/σ. Specifically, we derive results for λ/σ in terms of the packing fraction ϕ and the contact value of the distribution function $G(1)$.

We begin by deriving an exact expression for λ in the limit $\phi \to \phi_c$. Provided that $G(x)$ has the form (28) and that $G(1)$ diverges to infinity in the limit $\phi \to \phi_c$, an asymptotic analysis of the integral of (73) reveals that one has the equality

$$\frac{\lambda}{\sigma} = 1 + \frac{1}{D2^D\phi G(1)} \qquad \text{for } \phi \to \phi_c. \tag{74}$$

The remarkably simple form of expression (75) is note-

worthy. Observe that if $G(1)$ has the asymptotic form (26), then we have the following scaling law for the quantity $\lambda/\sigma - 1$:

$$\frac{\lambda}{\sigma} - 1 \sim (\phi_c - \phi)^s \qquad \text{for } \phi \to \phi_c. \qquad (75)$$

Next we derive rigorous upper bounds on λ (see also Ref. [35]). Specifically, since $G(x)$ is generally a monotonically increasing function of x for equilibrium ensembles of D-dimensional hard spheres [1], then we have the following upper bound on $E(x)$:

$$E(x) \leq \exp[-2^D \phi G(1)(x^D - 1)]. \qquad (76)$$

Substitution of (76) into (73) yields the upper bound

$$\frac{\lambda}{\sigma} \leq 1 + \int_1^\infty \exp[-2^D \phi G(1)(x^D - 1)]dx. \qquad (77)$$

The integral of (77) can be further simplified by transforming to the variable $u = x - 1$, giving

$$\frac{\lambda}{\sigma} \leq 1 + \int_0^\infty \exp[-2^D \phi G(1)(u^D + Du^{D-1} + \cdots + Du)]du. \qquad (78)$$

Since each term of the polynomial $u^D + Du^{D-1} + \cdots + Du$ is positive, the integral of (78) is bounded from above by retaining only the *linear term* Du, yielding the less restrictive inequality

$$\frac{\lambda}{\sigma} \leq 1 + \frac{1}{D2^D \phi G(1)}. \qquad (79)$$

The bound (79) can be written in terms of the reduced equation of state $p/\rho kT$ for equlibrium hard spheres via relations (18) and (19) as

$$\lambda \leq 1 + \frac{1}{2D(p/\rho kT - 1)}, \qquad (80)$$

where p is the pressure, T is absolute temperature, and k is Boltzmann's constant. For equilibrium hard rods ($D = 1$), we know that $G(x)$ is exactly given by $1/(1 - \phi)$ for $1 \leq x \leq \infty$ (see the Appendix) and hence the inequality (79) coincides with the exact result

$$\frac{\lambda}{\sigma} = 1 + \frac{1}{2\phi G(1)} = 1 + \frac{1 - \phi}{2\phi}. \qquad (81)$$

It is important to observe that the bound (79) becomes exact in the limit $\phi \to \phi_c$ [cf. (74)]. Elsewhere [35] it is shown that inequality (79) actually applies not only to equilibrium ensembles but to a certain class of ergodic nonequilibrium ensembles, such as the random sequential addition process [36].

Finally, we derive still weaker but general rigorous upper bounds on λ. Noting that $G_V(1/2) = (1 - \phi)^{-1} \leq G(x)$ for $1 \leq x \leq \infty$ for equilbrium hard spheres, one can employ inequality (79) to find that

$$\frac{\lambda}{\sigma} \leq 1 + \frac{1 - \phi}{D2^D \phi}. \qquad (82)$$

Observe that the bound (82) involves no approximation and turns out be valid not only for equilibrium ensembles but for a class of ergodic ensembles of isotropic hard spheres [35]. Of course, for hard rods ($D = 1$), expression (82) is exact [cf. (81)].

In the special case of an equilibrium ensemble of particles, the bound (81) can be written explicitly for $D = 3$ and $D = 2$ using the approximate results of the previous sections. The combination of (39), (40), and (81), gives for, $D = 3$,

$$\lambda \leq \begin{cases} 1 + \dfrac{(1 - \phi)^3}{24\phi(1 - \phi/2)}, & 0 \leq \phi \leq \phi_f \\ 1 + \dfrac{(\phi_c - \phi)}{24\phi g_f(1)(\phi_c - \phi_f)}, & \phi_f \leq \phi \leq \phi_c. \end{cases} \qquad (83)$$

Substitution of relations (59) and (60) into (81) yields, for $D = 2$,

$$\lambda \leq \begin{cases} 1 + \dfrac{(1 - \phi)^2}{8\phi(1 - 0.436\phi)}, & 0 \leq \phi \leq \phi_f \\ 1 + \dfrac{(\phi_c - \phi)}{8\phi g_f(1)(\phi_c - \phi_f)}, & \phi_f \leq \phi \leq \phi_c. \end{cases} \qquad (84)$$

Elsewhere [35] it is shown that for any ergodic ensemble of isotropic packings of identical, D-dimensional hard spheres, the mean distance obeys the inequality

$$\lambda \leq 1 + \frac{1}{D2^D \phi}. \qquad (85)$$

Thus any packing of identical, D-dimensional hard spheres in which the mean distance obeys the relation

$$\lambda > 1 + \frac{1}{D2^D \phi} \qquad (86)$$

cannot be ergodic and isotropic.

Figure 8 plots our prediction (thin solid line) of the dimensionless mean nearest-neighbor distance λ/σ for $D = 3$ as a function of the packing fraction ϕ. This is obtained through use of definition (73) and the relations (42) and (49). Our prediction is seen to be in excellent agreement with available simulation data (open circles) [32]. In the limit $\phi \to \phi_c = 0.64$, our prediction of λ/σ correctly goes to zero, in contrast with the TLR prediction in which λ/σ does not go to zero until $\phi \to 1$. It is interesting to note that the upper bound (77) is so sharp that it is indistinguishable from the result of (73) (solid line) on the scale of this figure. The upper bound (83) (thin dashed line of Fig. 8) is very sharp for packing fractions between freezing and random close packing and indeed becomes exact in the limit $\phi \to \phi_c$. The thick dashed and solid lines are the upper bounds (82) and (85), respectively. The shaded region is prohibited to ergodic, isotropic hard spheres according to (86).

In Table II we compare the mean nearest-neighbor distances for equilibrium hard spheres ($D = 3$), a face-centered-cubic lattice of spheres, and Poisson distributed (i.e., randomly overlapping) spheres. As expected, λ for equilibrium hard spheres lies between the corresponding distances for the other two systems. Although the
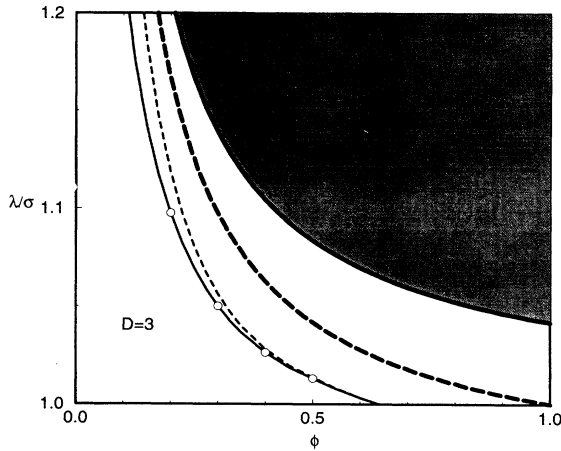
FIG. 8. Dimensionless mean nearest-neighbor distance λ/σ vs packing fraction ϕ for hard spheres ($D = 3$). The thin solid line is the equilibrium prediction obtained from (73), (42), and (49). Open circles are simulation data [32]. The thin dashed line is the upper bound (83). Thick dashed and solid lines are upper bounds (82) and (85), respectively. The shaded region is prohibited to ergodic, isotropic hard spheres according to (86).

mean nearest-neighbor distances for hard and overlapping spheres approach one another in the limit $\phi \to 0$, they diverge from one another as ϕ is increased. For example, at $\phi = 0.5$, λ for hard spheres is about twice as large as that of overlapping spheres. Note that the packing fraction for overlapping spheres is given by $\phi = 1 - \exp[-\rho v(\sigma/2)]$, where $v(\sigma/2)$ is the volume of a sphere [cf. (16)].

In Fig. 9 we depict our prediction (solid line) of the dimensionless mean nearest-neighbor distance λ/σ for $D = 2$ as a function of the packing fraction ϕ. This is ob-
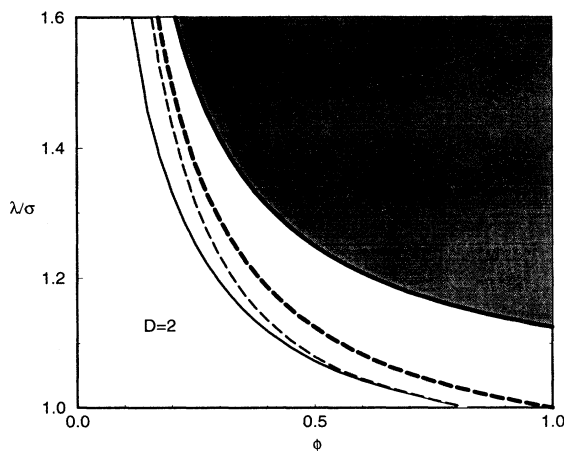

FIG. 9. Dimensionless mean nearest-neighbor distance λ/σ vs packing fraction ϕ for hard disks ($D = 2$). The thin solid line is the equilibrium prediction obtained from (73), (64), and (69). The thin dashed line is the upper bound (84). Thick dashed and solid lines are upper bounds (82) and (85), respectively. The shaded region is prohibited to ergodic, isotropic hard disks according to (86).

TABLE II. Dimensionless mean nearest-neighbor distance λ/σ for a face-centered-cubic lattice of spheres [$\lambda/\sigma = \pi^{1/3}/(3\sqrt{2}\phi)^{1/3}$], equilibrium hard spheres (83), and overlapping spheres ($\lambda/\sigma = \Gamma(4/3)/\{2[\ln(1 - \phi)]^{1/3}\}$).

| ϕ | Dimensionless mean nearest-neighbor distance λ/σ | | |
	Face-centered-cubic lattice	Equilibrium hard spheres	Overlapping spheres
0.10	1.949	1.221	0.945
0.20	1.547	1.098	0.736
0.30	1.351	1.050	0.630
0.40	1.228	1.026	0.559
0.50	1.140	1.013	0.505
0.60	1.073	1.003	0.460
0.64	1.050	1.000	0.443
0.70	1.019		0.420
0.74	1.000		0.404
0.80			0.381
0.90			0.338

tained through use of the definition (73) and the relations (64) and (69). Our prediction of λ/σ again correctly goes to zero in the limit that $\phi \to \phi_c = 0.82$. Again the upper bound (77) is so sharp that it is indistinguishable from the result of (73) (thin solid line) on the scale of this figure. The thin dashed line of Fig. 9 is the upper bound (84). The thick dashed and solid lines are the upper bounds (82) and (85), respectively. The shaded region is prohibited to ergodic, isotropic hard disks according to (86).

In Table III we compare the mean nearest-neighbor distances for three different two-dimensional systems: equilibrium hard disks, triangular lattice of disks, and Poisson distributed disks. The general trends described above for $D = 3$ apply here as well.

Table IV compares the mean nearest-neighbor distances for equilibrium hard rods ($D = 1$), periodic lattice of rods, and Poisson distributed rods. Note that the non-

TABLE III. Dimensionless mean nearest-neighbor distance λ/σ for a triangular lattice of disks $\{\lambda/\sigma = \pi^{1/2}/[(2\sqrt{3}\phi)^{1/2}]\}$, equilibrium hard disks (84), and overlapping disks ($\lambda/\sigma = \sqrt{\pi}/\{4[\ln(1 - \phi)]^{1/2}\}$).

| ϕ | Dimensionless mean nearest-neighbor distance λ/σ | | |
	Triangular lattice	Equilibrium hard disks	Overlapping disks
0.10	3.011	1.675	1.365
0.20	2.130	1.333	0.938
0.30	1.739	1.195	0.742
0.40	1.506	1.120	0.620
0.50	1.347	1.073	0.532
0.60	1.229	1.043	0.463
0.70	1.138	1.022	0.404
0.80	1.065	1.003	0.349
0.82	1.052	1.000	0.338
0.90	1.004		0.292
0.907	1.000		0.288

TABLE IV. Dimensionless mean nearest-neighbor distance λ/σ for a periodic lattice ($\lambda/\sigma = 1/\phi$), equilibrium hard rods [$\lambda/\sigma = (1 + \phi)/\phi$], and overlapping rods $\{\lambda/\sigma = 1/[2\ln(1 - \phi)]\}$.

ϕ	Dimensionless mean nearest-neighbor distance λ/σ		
	Periodic lattice	Equilibrium hard rods	Overlapping rods
0.10	10.000	5.500	4.746
0.20	5.000	3.000	2.241
0.30	3.333	2.167	1.402
0.40	2.500	1.750	0.979
0.50	2.000	1.500	0.721
0.60	1.666	1.333	0.546
0.70	1.429	1.215	0.415
0.80	1.250	1.125	0.311
0.90	1.111	1.056	0.217
1.00	1.000	1.000	0.000

ergodic lattice arrangement satisfies the inequality (86) for all $\phi < 0.5$.

VI. CONCLUSIONS

A simple form for the contact value of the radial distribution function $g(\sigma)$ is assumed between freezing and random close packing that incorporates a pole at the random close-packing density, enabling us to find simultaneously accurate and simple expressions for the nearest-neighbor functions of equilibrium hard spheres and disks and hence the mean nearest-neighbor distance λ. We made use of an important observation, namely, that the

functional nature of $g(\sigma)$ between dilute and freezing densities is fundamentally different from that between freezing and random close packing. Rigorous bounds on λ were also derived for D-dimensional hard spheres in equilibrium.

ACKNOWLEDGMENTS

APPENDIX: EXACT RESULTS FOR HARD RODS

The nearest-neighbor functions for hard rods ($D = 1$) at packing fraction ϕ were found exactly by TLR [18] using their series expansions. MacDonald [9] found the same expression earlier using a different approach. One has

$$E(x) = \exp\left[\frac{-2\phi(x - 1)}{1 - \phi}\right] \quad \text{for } x \geq 1, \quad \text{(A1)}$$

$$H(x) = \frac{2\phi}{1 - \phi}\exp\left[\frac{-2\phi(x - 1)}{1 - \phi}\right] \quad \text{for } x \geq 1, \quad \text{(A2)}$$

$$G(x) = \frac{1}{1 - \phi} \quad \text{for } x \geq 1. \quad \text{(A3)}$$

The case $D = 1$ may serve as a useful model of various types of layered media.

[1] H. Reiss, H. L. Frisch, and J. L. Lebowitz, J. Chem. Phys. **31**, 369 (1959).

[2] E. Hefland, H. L. Frisch, and J. L. Lebowitz, J. Chem. Phys. **34**, 1037 (1961). The scaled-particle theory of Ref. [1] for $D = 3$ is extended here to treat $D = 2$ and $D = 1$.

[3] F. H. Stillinger, E. A. DiMarzio, and R. L. Kornegay, J. Chem. Phys. **40**, 1564 (1964).

[4] J. D. Bernal, Proc. R. Soc. London Ser. A **280**, 299 (1964).

[5] J. L. Finney, Proc. R. Soc. London Ser. A **319**, 479 (1970).

[6] J. G. Berryman, Phys. Rev. A. **27**, 1053 (1983).

[7] H. Reiss and A. D. Hammerich, J. Phys. Chem. **90**, 6252 (1986).

[8] Y. Song, R. M. Stratt, and E. A. Mason, J. Chem. Phys. **88**, 1126 (1988).

[9] J. R. MacDonald, Mol. Phys. **44**, 1043 (1981).

[10] S. H. Simon, V. Dobrosavljevic, and R. M. Stratt, J. Chem. Phys. **94**, 7360 (1991).

[11] B. D. Lubachevsky and F. H. Stillinger, J. Stat. Phys. **60**, 561 (1990); **64**, 501 (1991).

[12] J. Rubinstein and S. Torquato, J. Fluid Mech. **206**, 25 (1989).

[13] S. Torquato and J. Rubinstein, J. Chem. Phys. **90**, 1644 (1989).

[14] S. Chandrasekhar, Rev. Mod. Phys. **15**, (1943).

[15] J. G. McNally and E. C. Cox, Development **105**, 323 (1989).

[16] I. A. Aksay, Ceramics Int. **17**, 267 (1991).

[17] P. Hertz, Math. Ann. **67**, 387 (1909).

[18] S. Torquato, B. Lu, and J. Rubinstein, Phys. Rev. A **41**, 2059 (1990).

[19] J. P. Hansen and I. R. McDonald, *Theory of Simple Liquids* (Academic, London, 1986).

[20] R. Zallen, *The Physics of Amorphous Solids* (Wiley, New York, 1983).

[21] A. E. Scheidegger, *The Physics of Flow Through Porous Media* (Macmillan, New York, 1960).

[22] S. Torquato and F. Lado, Phys. Rev. B **33**, 6428 (1986).

[23] S. Torquato and F. Lado, Proc. R. Soc. London Ser. A **417**, 59 (1988).

[24] M. Shahinpoor, Powder Technol. **25**, 163 (1980).

[25] B. A. Cornell, J. Middlehurst, and N. S. Parker, J. Colloid Interface Sci. **81**, 280 (1981).

[26] T. I. Quickenden and G. K. Tan, J. Colloid. Interface Sci. **48**, 382 (1974).

[27] In Ref. [18], the authors studied two different types of nearest-neighbor distribution functions (which depend on the location of the reference point): the so-called *particle* and *void* quantities. In the case of the "particle" quanti-

ties (the same functions studied in the present paper), the reference point is the center of a sphere. These quantities carried the subscript P in Ref. [18], but in the present work we omit this subscript. In the case of the "void" quantities, the reference point is any arbitrary point in the system; the nontrivial contribution to these functions involve points in the space exterior to the spheres (void space). The void functions were first studied by Reiss, Frisch, and Lebowitz [1] in their scaled-particle theory.

[28] It is widely accepted that an equilibrium hard-sphere system possesses a fluid-to-solid phase transition at the so-called "freezing point." This is supported by computer simulation studies (see Refs. [30] and [31]). Although there is presently no rigorous proof for the occurrence of such a phase transition, geometrical arguments have been put forth that strongly support its existence (see Ref. [7]). Above the freezing point, the fluid (or disordered) state can persist along the metastable branch, which is conjectured to end at the random close-packing density [see, e.g., E. J. Levre, Nature Phys. Sci. **20**, 235 (1972)].

[29] In an ensemble in which each member consists of N particles in a volume V, the n-particle probability density $\rho_n(\mathbf{r}_1, \ldots, \mathbf{r}_n)$ characterizes the probability of finding n particles with configuration $\mathbf{r}_1, \ldots, \mathbf{r}_n$. The ensemble is *ergodic* if ρ_n can be obtained from a single member of the ensemble. If the ensemble is ergodic, then statistical homogeneity is implied (ρ_n is translationally invari-

ant) and thus it is understood that the *thermodynamic limit* ($N \to \infty$, $V \to \infty$, such that N/V is equal to a fixed constant ρ) has been taken. (By contrast, note that statistical homogeneity does not imply ergodicity.) The ensemble is statistically isotropic if ρ_n is rotationally invariant.

[30] J. Tobochnik and P. M. Chapin, J. Chem. Phys. **88**, 5824 (1988).

[31] W. G. Hoover and F. H. Ree, J. Chem. Phys. **49**, 3609 (1968).

[32] S. Torquato and S. B. Lee, Physica A **167**, 361 (1990).

[33] For example, we also found an expression for $G(1)$ in the range $\phi_f \leq \phi \leq \phi_c$ by matching not only the value of the function $g^{-1}(1)$ at $\phi = \phi_f$ but its first derivative with respect to ϕ at $\phi = \phi_f$. The resulting nearest-neighbor functions differed negligibly from the expressions (41)–(43). We note that $g^{-1}(1)$ may indeed be nonanalytic in ϕ at $\phi = \phi_f$.

[34] S. Torquato, J. Chem. Phys. **81**, 5079 (1984); **84**, 6345 (1986).

[35] S. Torquato, Phys. Rev. Lett., **74**, 2156 (1995).

[36] B. Widom, J. Chem. Phys. **44**, 3888 (1966); J. Feder, J. Theor. Biol. **87**, 237 (1980); R. H. Swendsen, Phys. Rev. A **24**, 504 (1981); P. Shaaf and J. Talbot, Phys. Rev. Lett. **62**, 175 (1989); P. Viot, G. Tarjus, and J. Talbot, Phys. Rev. E **48**, 480 (1993).
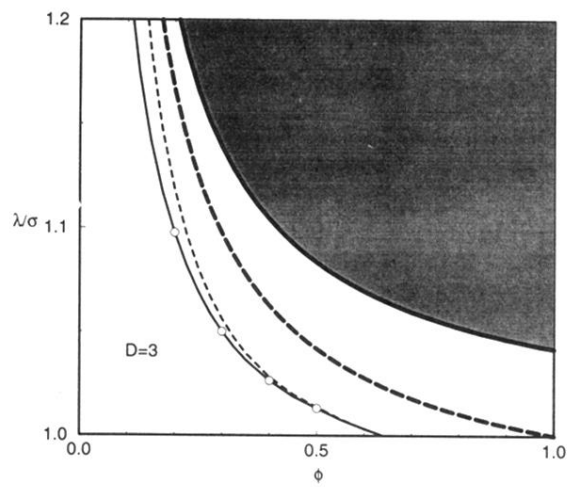
FIG. 8. Dimensionless mean nearest-neighbor distance λ/σ vs packing fraction ϕ for hard spheres ($D = 3$). The thin solid line is the equilibrium prediction obtained from (73), (42), and (49). Open circles are simulation data [32]. The thin dashed line is the upper bound (83). Thick dashed and solid lines are upper bounds (82) and (85), respectively. The shaded region is prohibited to ergodic, isotropic hard spheres according to (86).
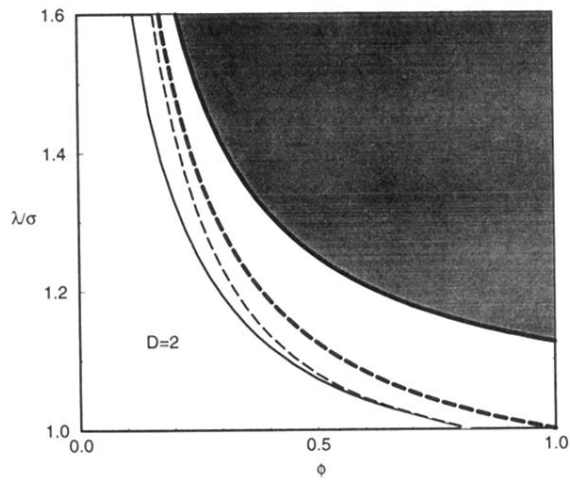
FIG. 9. Dimensionless mean nearest-neighbor distance λ/σ vs packing fraction ϕ for hard disks ($D = 2$). The thin solid line is the equilibrium prediction obtained from (73), (64), and (69). The thin dashed line is the upper bound (84). Thick dashed and solid lines are upper bounds (82) and (85), respectively. The shaded region is prohibited to ergodic, isotropic hard disks according to (86).